Appendix K. Method Development and Discussion of Analysis by Batelle Laboratory

Battelle
. . . Putting Technology To Work
505 King Avenue
Columbus, Ohio 43201-2693
Telephone (614) 424-6424
Facsimile (614) 424-5263

October 16, 2001

Dr Randy Segawa
Senior Environmental Research Scientist
California Environmental Protection Agency
Department of Pesticide Regulation
1001 I St
PO Box 4015
Sacramento, CA 95812-4015

Re: Final Report - Development of Methods for the Extraction and Analysis of Air Samples for Selected Pesticides Collected on XAD-4.
CDPR Agreement 99-0245.

Dear Randy:

Enclosed are two copies of the Final Report for the Development of Methods for the Extraction and Analysis of Air Samples for Selected Pesticides Collected on XAD-4, CDPR Agreement 99-0245. I have added the information you requested on the trapping/extraction efficiency experiment. If you have any further questions, please contact me either by phone at 614-424-7210 or by email at kennyd@battelle.org.

Sincerely,

Donald V. Kenny
Principal Research Scientist
Atmospheric Science and
Applied Technology Department

DVK:llg

Enclosures

Development of Methods for the Extraction and Analysis of Air Samples for Selected Pesticides Collected on XAD-4

For

California Department of Pesticide Regulation
Agreement 99-0245

By

Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201

October 16, 2001

Introduction

Battelle proposed to develop an extraction and LC/MS/MS method for the analysis of selected pesticides from air samples. The California Department of Pesticide Regulation (CADPR) selected XAD-4 as the sampling medium. The CAPDR also indicated that 30 mL of XAD-4 would be used in the samplers, and that the air would be sampled at 30 L/min for 24 hour sampling periods. With this sampling framework as a background, Battelle conducted the study that is summarized in the following report.

List of Target Analytes

A number of target analytes were of interest to the CADPR. Table 1 shows the initial list of target analytes.

Table 1. Initial List of Target Analytes.

Target Analyte List	
High Priority Analytes	**Medium Priority Analytes**
Benomyl	Acephate
Methomyl	Anilazine
Oxamyl	Dichlorvos (DDVP)
Thiodicarb	Ethephon
Thiophanate-methyl	Maneb
	Methamidophos

Battelle proposed to develop a method for the extraction and analysis of 5 high priority analytes (benomyl, methomyl, oxamyl, thiodicarb, and thiophanate-methyl) and, if possible, 6 medium priority analytes (acephate, analizine, DDVP, ethephon, maneb and methamidophos). During the course of the program, Battelle was also asked to evaluate an additional analyte, ethylene thiourea (ETU).

Task 1. Method Development for Analysis of Selected Pesticides

The method development and validation included the following sub-tasks:

- Determine "best" ionization mode and conditions for analytes
- Obtain MS/MS spectrum for each target analyte
- Select 2 - 3 precursor/fragment ion transitions for selected ion monitoring experiments
- Develop chromatographic method using selected ion transitions
- Determine laboratory detection limits and quantitation limits using the EPA Method (40 CFR, Part 136, Appendix B)

MS/MS Spectra of the Target Analytes

All of the target analytes were first tested using positive and negative ion atmospheric pressure chemical ionization (APCI) modes. The target analytes were then tested using positive and negative ion electrospray ionization (ESI) modes. Each ionization mode takes advantage of the physical/chemical properties of the molecules.

For logistical reasons two different triple quadrupole tandem mass spectrometers (PE/Sciex API-365 and Micromass Quattro LC) were used to obtain daughter ion spectra for the target analytes. To obtain MS/MS spectra for each of the target analytes, a 100 ng/mL solution in a 50/50 mix of water (20 mM formic acid)/methanol (20 mM formic acid) system was prepared. The standard was infused into the ion source of the mass spectrometer using a syringe drive (typically at a rate on the order of 100 μL/min). The parent or precursor ion was determined by scanning the first mass-analyzing quadrupole over a mass range of +/- 20 amu of the molecular weight of the target analyte. A list of the parent ions for the target analytes can be found in Table 2. Once the parent ion was identified (typically M+1) a daughter or fragment ion spectrum was obtained. The daughter ion spectrum was obtained by setting the first mass-analyzing quadrupole transmit only the parent ion of interest. The second quadrupole was set in the rf only, or all-pass mode, and the collision gas (N_2 or Ar, depending on the specific mass spectrometer) in the collision cell. The resulting daughter or fragment ions were then identified by the third quadrupole (second mass-analyzing quadrupole). The entrance and collision energies were then optimized to produce the most intense signal for each of the daughter ions produced. The daughter ions associated with each of the target analytes are shown in Table 2.

Daughter ion spectra obtained using the PE/Sciex API-365 for the target analytes are summarized in Appendix A and the daughter ion spectra obtained using the Micromass Quattro LC for the target analytes are summarized in Appendix B. Similar MS/MS spectra were obtained using both instruments, and intensities for individual daughter ions were maximized by optimizing the

Table 2. Summary of Data on Target Analytes

Target Analyte	Ionization Mode	Parent Ion	Daughter Ions	Retention time (min)	Instrument Detection Limits (ng/mL)[1]	Instrument Detection Limits (ng/m^3)[2]	Extraction Efficiencies (%)	Extraction Efficiencies Post Sampling[2,4] (%)
Benomyl	+ ESI	291	192, 160	9.16	5.7	0.26	ND[3]	ND[3]
MBC	+ ESI	192	160, 132	2.48	3.7	0.17	37 ± 5	8 ± 9
2-AB	+ ESI	134	92, 65	2.05	1.9	0.09	30 ± 2	3 ± 2
Methomyl	+ ESI	163	88, 106	2.97	2.5	0.12	120 ± 14	26 ± 16
Oxamyl	+ ESI	220	72, 90	2.75	2.6	0.12	101 ± 10	Interference[5]
Thiodicarb	+ ESI	355	88, 193	6.52	4.9	0.21	173 ± 17	Interference[5]
Thiophanate-methyl	+ ESI	343	151, 311	5.52	6.0	0.28	9 ± 1[3]	ND[3]
Acephate	+ ESI	184	95, 49, 143,	2.72	4.7	0.22	136 ± 49	Interference[5]
Methamidophos	+ ESI	142	94, 125	2.72	2.9	0.13	66 ± 10	17 ± 11
ETU	+ ESI	103	103, 44	2.65	2.0	0.09	5 ± 1	Interference[5]
Anilizine	- ESI	273/275	151,35/153,37	--	--	--	--	--
DDVP	- ESI	205/207	111/113	--	--	--	--	--
Ethephon	- ESI	143/145	79	--	--	--	--	--
Maneb	NA	NA	NA	--	--	--	--	--

1 Using Method described in 40 CFR Appendix B

2 Using CADPR sampling parameters of 30 L/min for 24 hours

3 Benomyl and thiophanate-methyl degrade into MBC and 2-AB

4 Results based on single set (three replicates) of experiments - Battelle directed to stop work prior to completion of repeat set of experiments.

5 Interference observed for these analytes - Quantitation of multiple parent/daughter ion transitions did not agree.

different ion optics of each mass spectrometer.

The approach adopted in the method development activities was to concentrate on the high priority analytes, then include as many medium priority compounds as possible. Table 2 summarizes the initial data obtained for the target analytes. Compounds of interest on the initial list but not included in Table 2 are analizine, DDVP, ethephon and maneb.

These initial experiments to obtain MS/MS spectra showed that benomyl and thiophanate-methyl degrade easily in solution as well as in the ion source of the mass spectrometer. The breakdown products are well known and have been identified as carbendazim (MBC) and 2-aminobenzimidazol (2-AB).[1, 2, 3, 4, 5] These analytes were treated as high priority analytes, as they will provide information about the overall benomyl and thiophanate-methyl concentration in the samples.

Two parent ions are listed for analizine, DDVP and ethephon. Each of these pesticides contain at least 1 chlorine atom, so the two ions listed each time account for the two naturally occurring isotopes at m/z 35 and 37.

Liquid Chromatographic Method for the Analysis of the Target Analytes

Because the target analyte list comprises of several different classes of compounds, baseline resolution of the target analytes was not achieved. This is not a deterrent to the analysis methodology, since the power of MS/MS can be used to "separate" peaks that may co-elute chromatographically. The liquid chromatography for the target analytes was optimized using a water (20mM formic acid)/ methanol (20 mM formic acid) system. The time table below shows the solvent gradient used.

Column - Supelco Discovery C8 15cm X 4.6 mm X 5 μm
Solvent A - 20 mM Formic Acid in H_2O
Solvent B - 20 mM Formic Acid in Methanol
Flow - 0.8 mL/min

Time	Solvent A %	Solvent B %
0.00	50	50
2.00	50	50
7.00	5	95
10.0	5	95
15.0	50	50

Appendix C shows the total ion chromatogram (TIC), and the selected ion chromatograms (SIC) for the target analytes for a 100 ng/mL standard.

For analizine and DDVP an MS/MS daughter ion spectrum was obtained. However analizine and DDVP were medium priority compounds and not included in further method development efforts because all of the compounds in Table 2 were analyzed by positive ion electrospray ionization, whereas these compounds require negative ion electrospray ionization for optimum analysis. Analyses for these compound would require a separate LC/MS/MS analysis.

For ethephon, an MS/MS daughter ion spectrum was obtained. However, in addition to requiring negative ion electrospray ionization, ethephon being a phosphonic acid, would also require a different

extraction procedure than the high priority analytes. Since it was listed as a medium priority analyte, it was not included in subsequent methods development activities.

No MS or MS/MS spectra could be obtained for maneb. Research into existing extraction and analysis methodologies for maneb suggest that OSHA Method 107 can be used to analyze air samples for this analyte as well as other manganese containing pesticides. (This method is described on OSHA's web site at www.osha-slc.gov/dts/sltc/methods/organic/org107/org107.html) This method requires an extraction with 5% cysteine and 5% EDTA, followed by analysis using ion chromatography and UV detection. This method is incompatible with the methods used for the high priority analytes. Therefore, no further work was done on maneb.

Task 2. Method Development for the Extraction of Pesticides from XAD-4

Extraction of XAD-4 for the Target Analytes

All extraction procedures were performed using XAD-4 resin provided to Battelle by the CAPDR. All lots of resin received by Battelle were cleaned by CADPR personnel prior to shipment to Battelle.

The first procedures attempted for the extraction of the high priority target analytes from the XAD-4 used Soxhlet extraction methodologies. The solvents used were methanol (MeOH), acetonitrile (ACN), acetone (ACE), and dichloromethane (DCM). The extracts were concentrated using a Kaderna-Danish apparatus and nitrogen blow-down methods. These procedures resulted in degradation, extensive losses, and erratic results for many of the target analytes, as shown in the results in Table 3. Methanol and acetone only recovered 2 of the 5 high priority target analytes, while acetonitrile recovered 3 of the 5 target analytes. Although DCM was able to recover 4 of the 5 target analytes, erratic results were obtained since the DCM had to be blown to dryness then re-constituted into a more LC-compatible solvent.

In an effort to increase recoveries, we reduced the extraction time, solvent volumes, and solvent concentration steps, as a result 30 mL samples of XAD-4 were extracted using a Dionex ASE 200 Accelerated Solvent Extractor. With acetonitrile as the solvent, samples were extracted at 1500 psi, 80°C, 5 minute hold time, and 100% rinse in three steps. The extract (40 mL - 50 mL) was then concentrated to 2 mL using a Kaderna-Danish apparatus. The 2 mL extract was further concentrated to 0.5 mL under a gently stream of nitrogen, then reconstituted in the 50/50 water (20mM formic acid)/methanol (20 mM formic acid) system. Extraction efficiencies are shown in Table 2.

Acceptable recoveries were achieved for methomyl, oxamyl, thiodicarb, acephate and methamidophos. Both benomyl and thiophanate-methyl degraded during the extraction and concentration steps to MBC and 2-AB. The initial acetonitrile extraction was unable to efficiently remove the MBC or 2-AB. A second extraction of the same cartridge with acetone following the acetonitrile extraction did however remove the MBC and 2-AB.

A set of trapping/extraction efficiency experiments was performed. Target analytes were spiked on to 30 mL of XAD-4 and air was passed through the cells at 30 L/min for 24 hours to simulate field

sampling conditions. The results are shown in Table 2. In general, the results of these experiments showed poor recoveries. As expected, benomyl and thiophante-methyl were not detected (degradation to MBC and 2-AB). MBC and 2-AB were recovered at 8% and 3% respectively. Recoveries for methomyl and methamidophos were 26% and 17% respectively. In addition to the poor recoveries, interferences were observed for oxamyl, thiodicarb, acephate and ETU. Although the mass spectrometer was operated in the MS/MS mode, interferences with one or more of the parent/daughter ion transitions was observed. These interferences prevented accurate quantitation.

Battelle was not convinced that the results from the first set of experiments were truly representative of the analytical methodology. Because of the difficulties encountered with this set of experiments, Battelle was in the process of repeating these trapping/extraction efficiency experiments when the client instructed Battelle to stop work before results could be obtained.

Table 3. Results from Soxhlet Extraction/Kaderna-Danish Concentration Using Different Solvents

Compound	Solvent			
	MeOH	ACN	ACE	DCM
Benomyl	63 ± 3	41 ± 20	27 ± 7	80 ± 27
Methomyl	23 ± 5	24 ± 8	< 20 %	33 ± 22
Oxamyl	< 20 %	< 20 %	< 20 %	22 ± 3
Thiodicarb	< 20 %	25 ± 9	77 ± 4	< 20 %
Thiophanate-methyl	< 20 %	< 20 %	< 20 %	22 ± 13

- n=3
- Recoveries < 20 % were not acceptable and specific recoveries were not calculated.

Instrument Detection Limits

Instrument detection limits were calculated using the method described in 40 CFR Appendix B. Here, 7 replicates of a 10 ng/mL standard were analyzed and detection limits calculated using the procedure outlined in the CFR. The results are shown in Table 2. The detection limits ranged from 1.9 ng/mL to 6.0 ng/mL.

Method Detection Limits

Method detection limits were calculated using the procedure described in 40 CFR Appendix B. Here, 7 replicates of a standard were spiked onto 30 mL of the XAD-4 and extracted. The final extract concentration was expected to be 100 ng/mL The extracts were analyzed and the method detection limits were calculated using the procedure outlined in the CFR. The method detection limits for the target analytes ranged from "not detected" for benomyl and thiophanate-methyl to 86 ng/mL for oxamyl. The results of these experiments are shown in Table 4.

Table 4. Method Detection Limits for Target Analytes

Target Analyte	Method Detection Limit[4] (ng/mL)	Method Detection Limit (ng/m^3)
Benomyl	ND[1]	--
MBC	38	1.8
2-AB	15	0.7
Methomyl	33	1.5
Oxamyl	86	4.0
Thiodicarb	26	1.2
Thiophanate-methyl	ND[1]	--
Acephate[2]	37	1.7
Methamidophos	23	1.1
ETU[3]	40	1.9

1 Degrades into MBC and 2AB
2 Over-recoveries observed - MDL is statistical anomaly
3 Single ion - blank contamination also observed
4 Using method described in 40 CFR Appendix B

Stability Study

Experiments were performed to determine the effect of storage on the stability of the target analytes over a one-month period. Analyses were performed at 0, 15, and 26 days. In the first experiment, two sets of XAD-4 samples (30 mL) were spiked with 2 cocktails. The first set of XAD-4 samples was spiked with a cocktail containing benomyl, methomyl, oxamyl, thiodicarb, thiophanate-methyl, acephate, methamidophos, and ETU. The second set of was spiked with a cocktail containing the benomyl, thiophanate-methyl breakdown/degradation products MBC and 2-AB. (It was necessary to separate the degradation products from parent compound to determine the stability of all four target analytes.)

In the second experiment, the stability of the extracts was studied. Extracts from spiked XAD-4 samples were stored and analyzed on the designated days intervals. All of the samples (spiked XAD-4 and extracts) were stored at -20° C during the study. The results from the stability study are shown in Table 5.

Table 5. Stability Study Results

Target Analyte	Percent Recoveries ± Standard Deviation (n=3) Day 0	Day 15	Day 26
Benomyl	0	0	0
MBC	37 ± 5	11 ± 2 extraction of Mix A[1] 21 ± 3 extraction of Mix B[2]	67 ± 6 extraction of Mix A[1] 92 ± 10extraction of Mix B[2]
2-AB	30 ± 2	3 ± 1 extraction of Mix A[4] 22 ± 7 extraction of Mix B	43 ± 22 extraction of Mix A 32 ● 3 extraction of Mix B
Methomyl	120 ± 14	69 ± 5	80 ± 5
Oxamyl	101 ± 10	91 ± 9	76 ± 1
Thiodicarb	173 ± 17	92 ± 1 (n=2) 72 ± 36 (n=3)	109 ± 20
Thiophanate-methyl	9 ± 1	16 ± 18	15 ± 17
Acephate	136 ± 49	529 ± 45	See below[3]
Methamidophos	66 ± 10	61 ± 4	63 ± 1
ETU	5 ± 1	2 ± 2	61 ± 13

1 Mix A - Benomyl, methomyl, oxamyl, thiodicarb, thiophanate-methyl, acephate, methamidophos, ETU

2 Mix B - MBC, 2-AB (Two mixes were used to distinguish between the spiking and subsequent degradation of benomyl/thiophanate-methyl on the XAD, and the spiking and retention of the breakdown products (MBC, 2-AB).)

3 Very high recoveries were obtained (>>>100%).

4 Same concentrations as found in the blank

As observed in the previous extraction tests, benomyl essentially degrades completely and thiophanate-methyl degrades significantly. Recoveries of MBC and 2-AB were erratic especially in Mix A, due to the degradation of benomyl and thiophanate-methyl.

Methomyl, oxamyl, thiodicarb, and methamidophos showed acceptable recoveries over the period of the stability test.

Very high recoveries were obtained (>>>100%) for acephate. It is believed that the acephate degrades in the stock solution used to prepare the standards. Low standard area counts inflate the recovery information.

An interference was observed in the 103/44 ion transition for ETU. Using the 103/103 ion transition, very low recoveries were obtained for Day 0 and Day 15 analyses. On Day 26, ETU was 61% recovered but showed a high standard deviation.

Conclusions

MS/MS daughter ion spectra were obtained for benomyl, MBC, 2-AB, methomyl, oxamyl, thiodicarb, thiophanate-methyl, acephate, methamidophos, ETU, anilizine, DDVP and ethephon. No MS or MS/MS daughter ion spectrum was obtained for maneb.

A LC/MS/MS method was developed for the analysis of ETU, 2-AB, methamidophos, methomyl, acephate, MBC, oxamyl, benomyl, thiophanate-methyl, and thiodicarb, with instrument detection limits ranging from 1.9 ng/mL to 6.0 ng/mL.

Method detection limits for the target analytes ranged from "not detected" for benomyl and thiophanate-methyl (degradation to 2-AB and MBC) to 86 ng/mL (4.0 ng/m^3) for oxamyl.

Initial extraction of the XAD-4 using Soxhlet extraction methods and Kaderna-Danish solvent concentration steps did not show acceptable recoveries. Extraction of the XAD-4 using the ASE extraction and Kaderna-Danish solvent concentration methods yielded recoveries ranging from 5% to 173%.

Degradation of benomyl and thiophanate-methyl into MBC and 2-AB occurred with both the Soxhlet extraction and ASE methodologies.

A set of trapping/extraction efficiency experiments showed poor recoveries. Recoveries ranged from not detected (benomyl and thiophanate-methyl) to 26% (methomyl). In addition, interferences were observed for oxamyl, thiodicarb, acephate, and ETU. Although the mass spectrometer was operated in the MS/MS mode, interferences with one or more of the parent/daughter ion transitions was observed.

Battelle was not convinced that the results from the first set of trapping/extraction efficiency experiments were truly representative of the analytical methodology. Because of the difficulties encountered with this set of experiments, Battelle was in the process of repeating these trapping/extraction efficiency experiments when the client instructed Battelle to stop work. Results from this second set of experiments were therefore not obtained.

Previous work by the California Air Resources Board (CARB)[6] has shown that benomyl and cabendazim (MBC) could be extracted off milligram quantities of XAD-2. This method is capable of analyzing extracts containing benomyl in the part per million (ppm) concentration range, but will not chromatographically separate benomyl from MBC..

The CARB work is fundamentally different from the experiments performed in this study, in the concentration of the final extracts, the sampling media, and the volume of sampling media used. The CARB work used XAD-2, which has a much smaller surface area than the XAD-4 provided to Battelle. The higher surface area of XAD-4 may aid in the capturing of ultra-trace levels of target species, but also it appears to adversely affect the extraction of these same species.

Because the CARB method uses only milligram quantities of sampling media, no solvent concentration steps were necessary. Battelle was contracted to analyze extract concentrations in the parts per billion (ppb) range (1000 times less than the CARB method) and extract much larger amounts of sampling media. By using 30 mL volumes of XAD-4, (~ 9.2 g) larger solvent volumes were necessary for extraction, thus requiring solvent concentration steps. In these concentration steps, losses of the target analytes can occur via evaporation and/or degradation. In addition the method developed in this study was able to chromatographically separate benomyl and thiophante-methyl from their degradation products, 2-AB and MBC.

Although CADPR felt that the method detection limits achieved in this study were greater than those desired for the overall Lompoc program, a method was successfully developed for the analysis of ng/mL (ng/m^3) levels of the target analytes. If ultra-trace levels of these target analytes are to be analyzed in air samples, it is recommended that the sample collection media be changed from XAD-4 to XAD-2 and/or poly-urethane foam (PUF) to improve extraction efficiency. It is also recommended that the volume of sampling media be minimized in order to minimize the volume of solvent solvent needed for extraction thereby minimizing the possible sample losses during the concentration steps.

References

1. Sandahl, M., Mathiasson, L., Jonsson, J. A., "Determination of thiophanate-methyl and its metabolites at trace level in spiked natural water using the supported liquid membrane extraction and the microporus membrane liquid-liquid extraction techniques combined on-line with high-performance liquid chromatography", *J. Chromatogr. A.*, 893, 123-131, 2000.

2. Atten, C. F., Bourke, J. B., Marafioti, R. A., "Determination of thiophanate-methyl as carbendazin by high-pressure liquid chromatography: application to onions and cabbage", *J. Agric. Food Chem.*, May-June, 30(3), 610-611, 1982.

3. Okita, Satoshi, Ishii, Y., Yun, S., "Determination of carbendazim and thiabendzole in environmental water samples using solid-phase extraction and LC/electrospray MS/MS", *Bunseki Kagaku*, 50(2) 127-132, 2001.

4. Marvin CH, Brindle ID, Hall CD, Chiba M, "Rapid on-line precolumn high-performance liquid chromatographic method for the determination of benomyl, carbendazim and aldicarb species in drinking water", *J Chromatogr.* Aug 30;555(1-2):147-154, 1991.

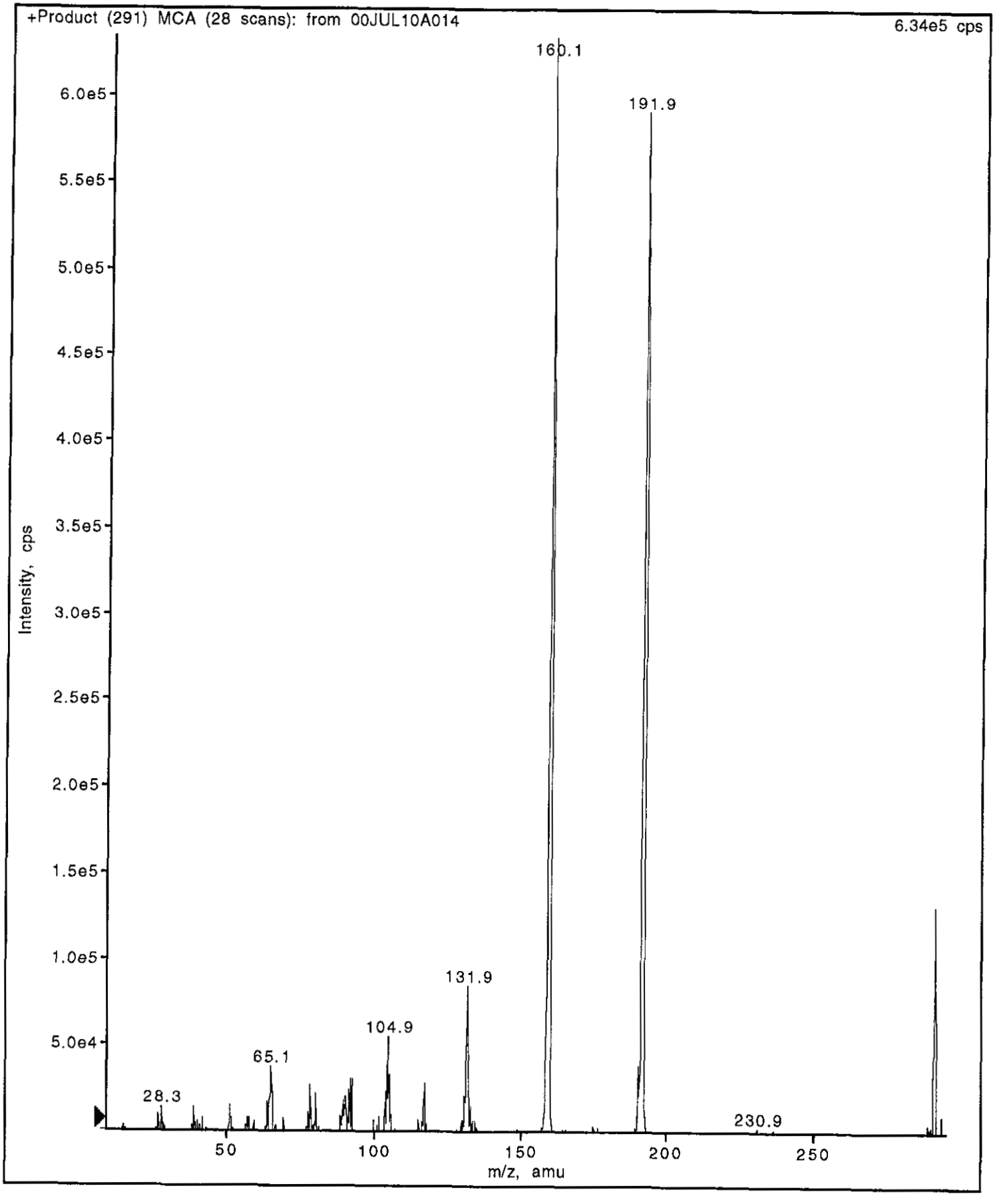
5. Jin, L., Bramble, F. Q., Pentz, A., Johnson, T., Dtermination of MBC/2-AB residues in various crops using liquid chromatography/electrospray ion trap MS/MS", Proceedings from the 48th ASMS Conference on Mass Spectrometry and Allied Topics, June 11-15, 2000, Long Beach, California.

6. State of California Air Resources Board Monitoring & Laboratory Division, SOP No. NLB021, "Standard Operating Procedure for the Determination of Benomyl and Its Breakdown Product, Carbendazim, in Ambient Air". March 18, 1988.

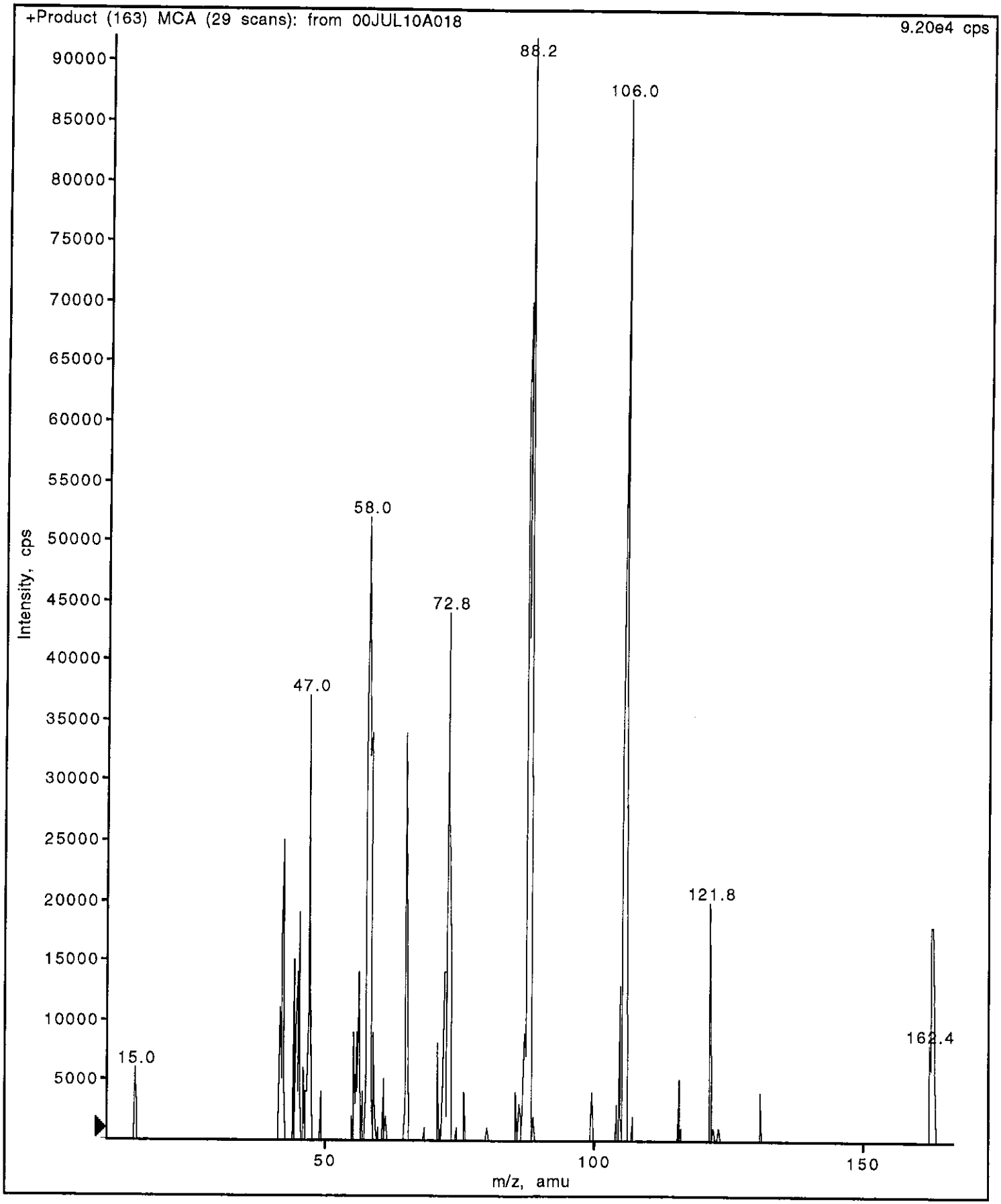
Appendix A

MS/MS Daughter Ion Spectra of Target Analytes
API-365

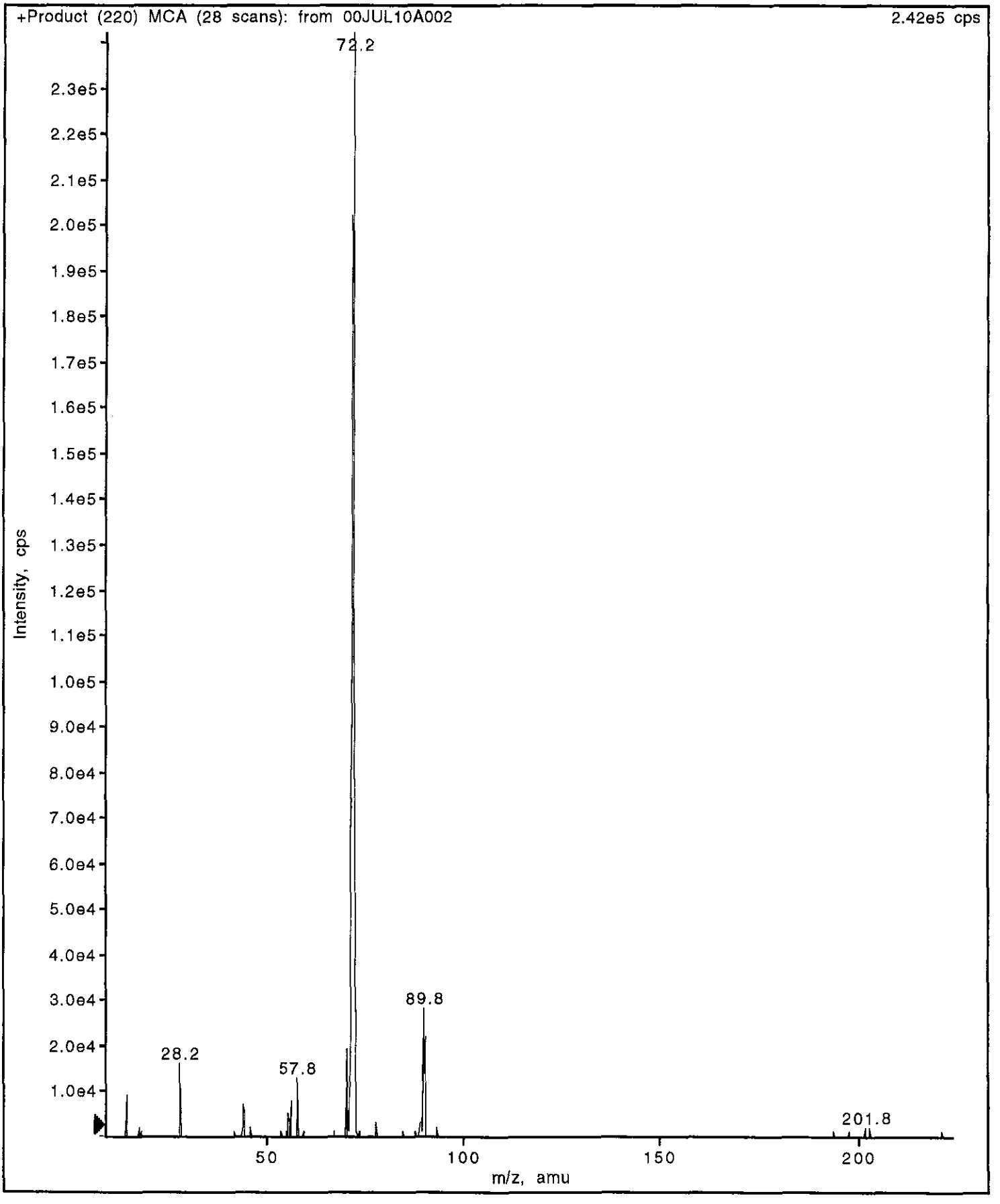
00JUL10A014 (- User: RAP3 - Compound: BENOMYL)
Period 1, Expt. 1; Mass range: 9.9 to 295.3 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Mon, Jul 10, 2000 at 15:43:11; Exp. Comment: BENOMYL 290.2 MS/MS Experiment



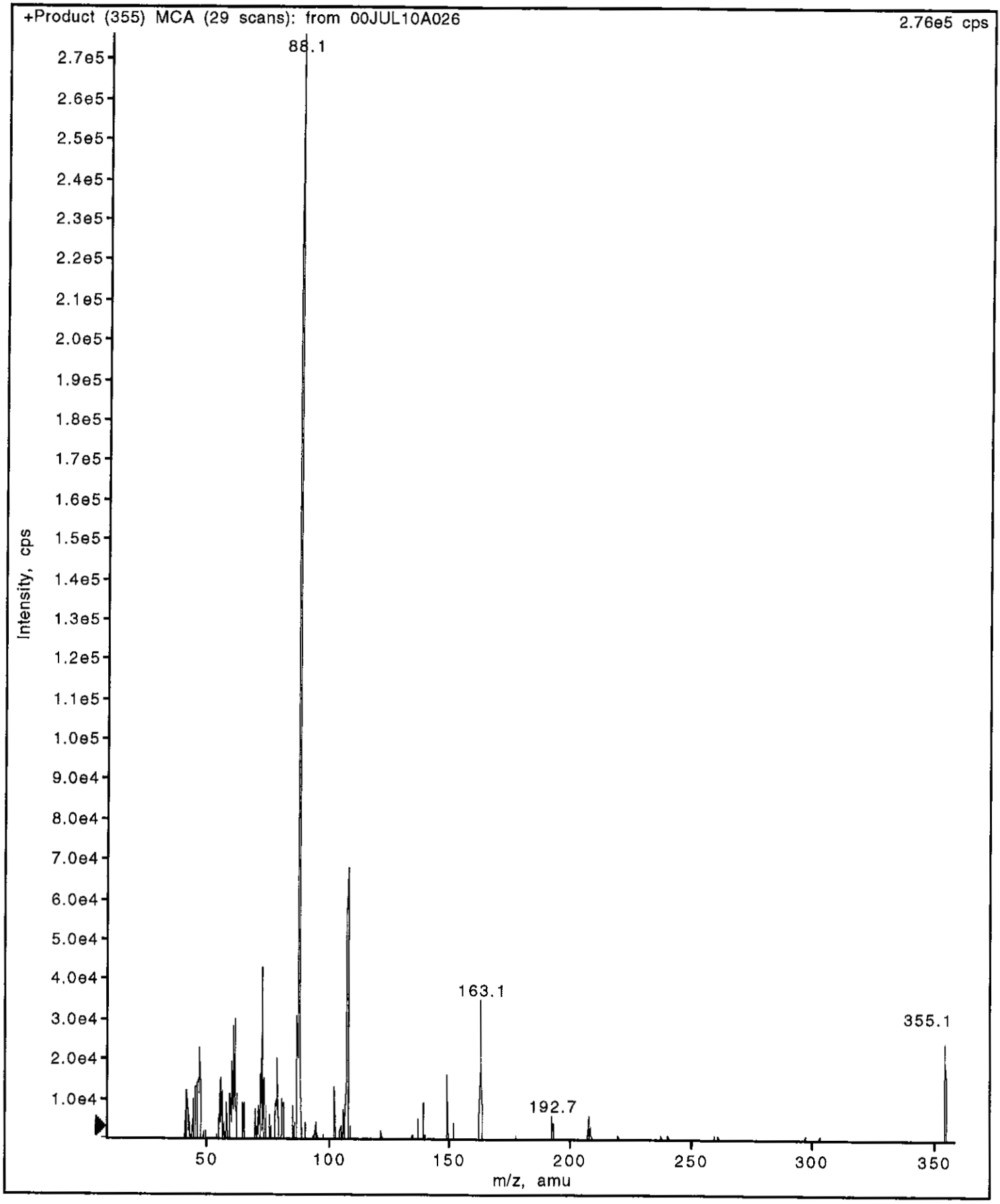
00JUL10A018 (- User: RAP3 - Compound: METHOMYL)
Period 1, Expt. 1; Mass range: 10.0 to 167.0 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Mon, Jul 10, 2000 at 16:05:11; Exp. Comment: METHOMYL 161.9 MS/MS Experiment



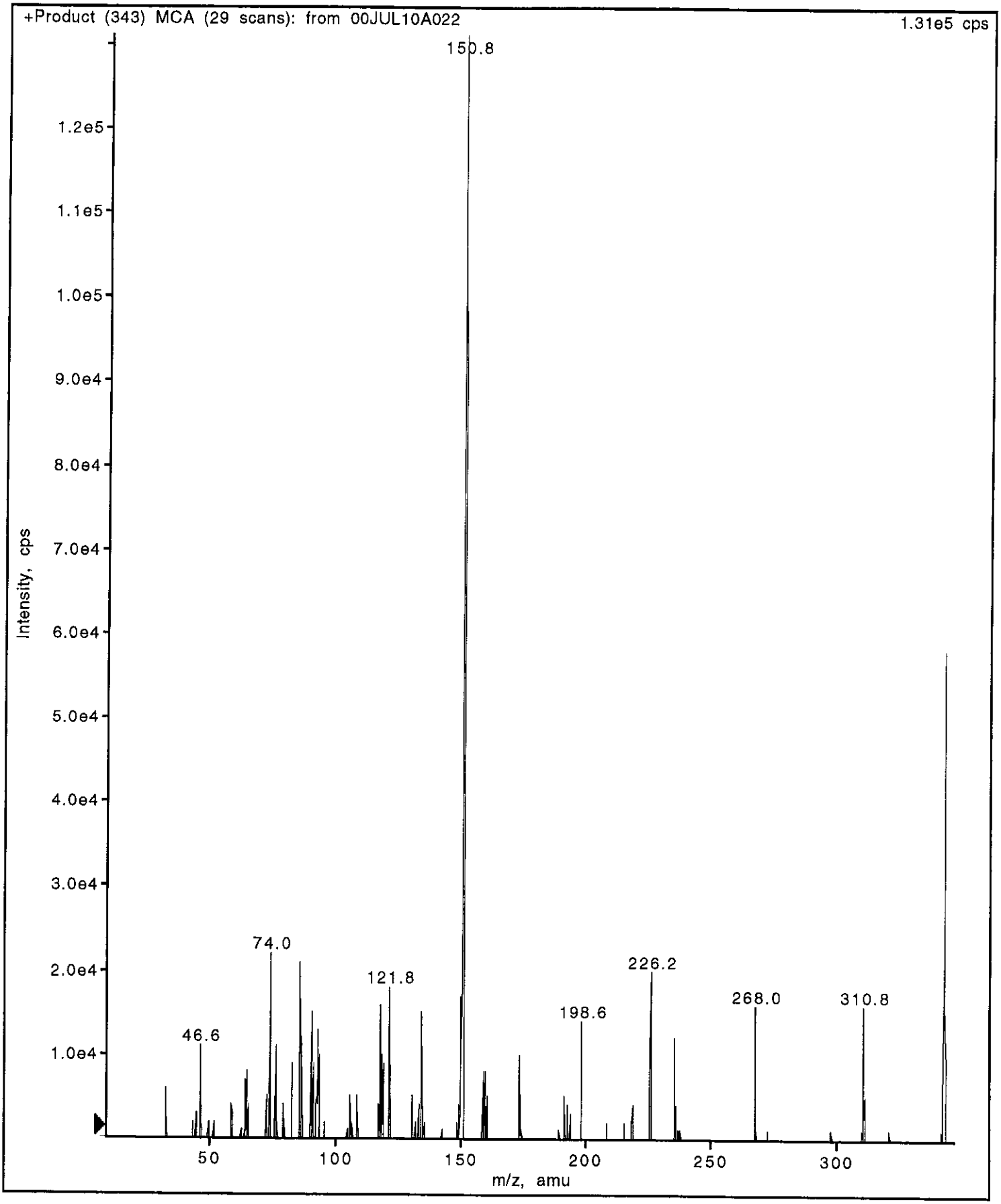
00JUL10A002 (- User: RAP3 - Compound: OXAMYL)
Period 1, Expt. 1; Mass range: 10.0 to 224.2 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Mon, Jul 10, 2000 at 14:21:42; Exp. Comment: OXAMYL 219.1 MS/MS Experiment



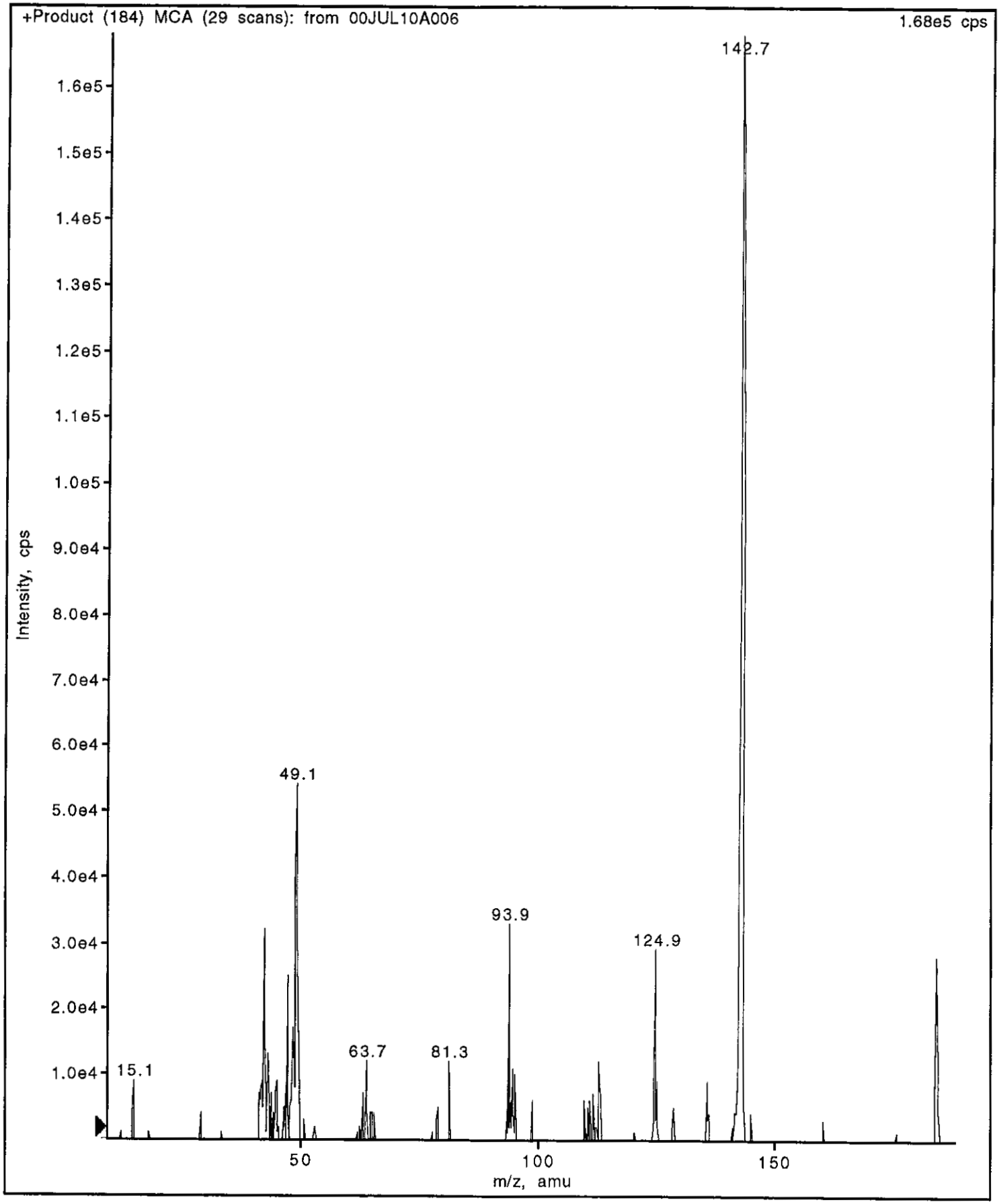
00JUL10A026 (- User: RAP3 - Compound: THIOIDICARB)
Period 1, Expt. 1; Mass range: 9.9 to 359.1 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Mon, Jul 10, 2000 at 16:43:06; Exp. Comment: THIOIDICARB 354.0 MS/MS Experiment



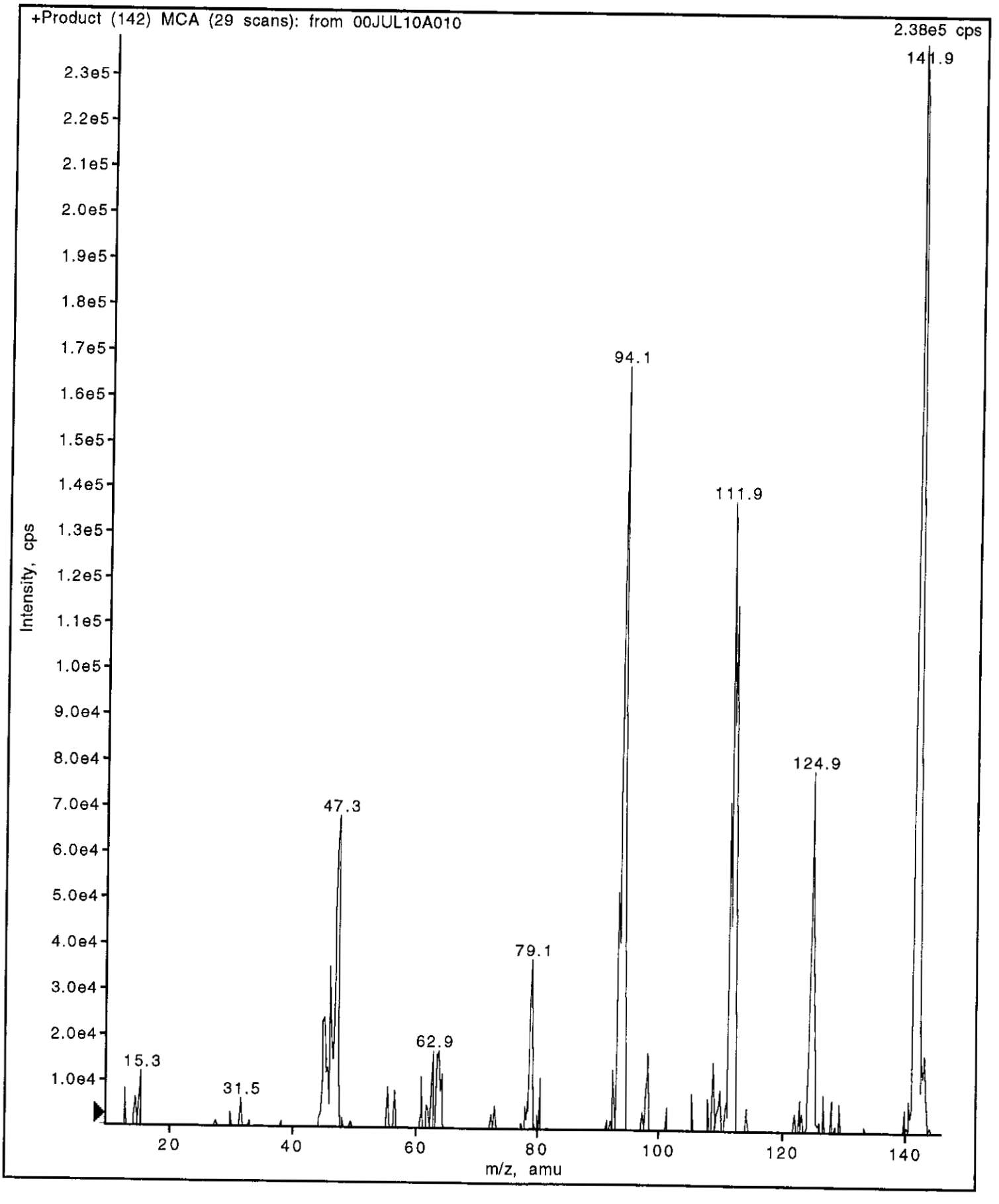
00JUL10A022 (- User: RAP3 - Compound: THIOPHANATE METHYL)
Period 1, Expt. 1; Mass range: 10.0 to 347.2 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Mon, Jul 10, 2000 at 16:27:13; Exp. Comment: THIOPHANATE METHYL 342.1 MS/MS Experiment



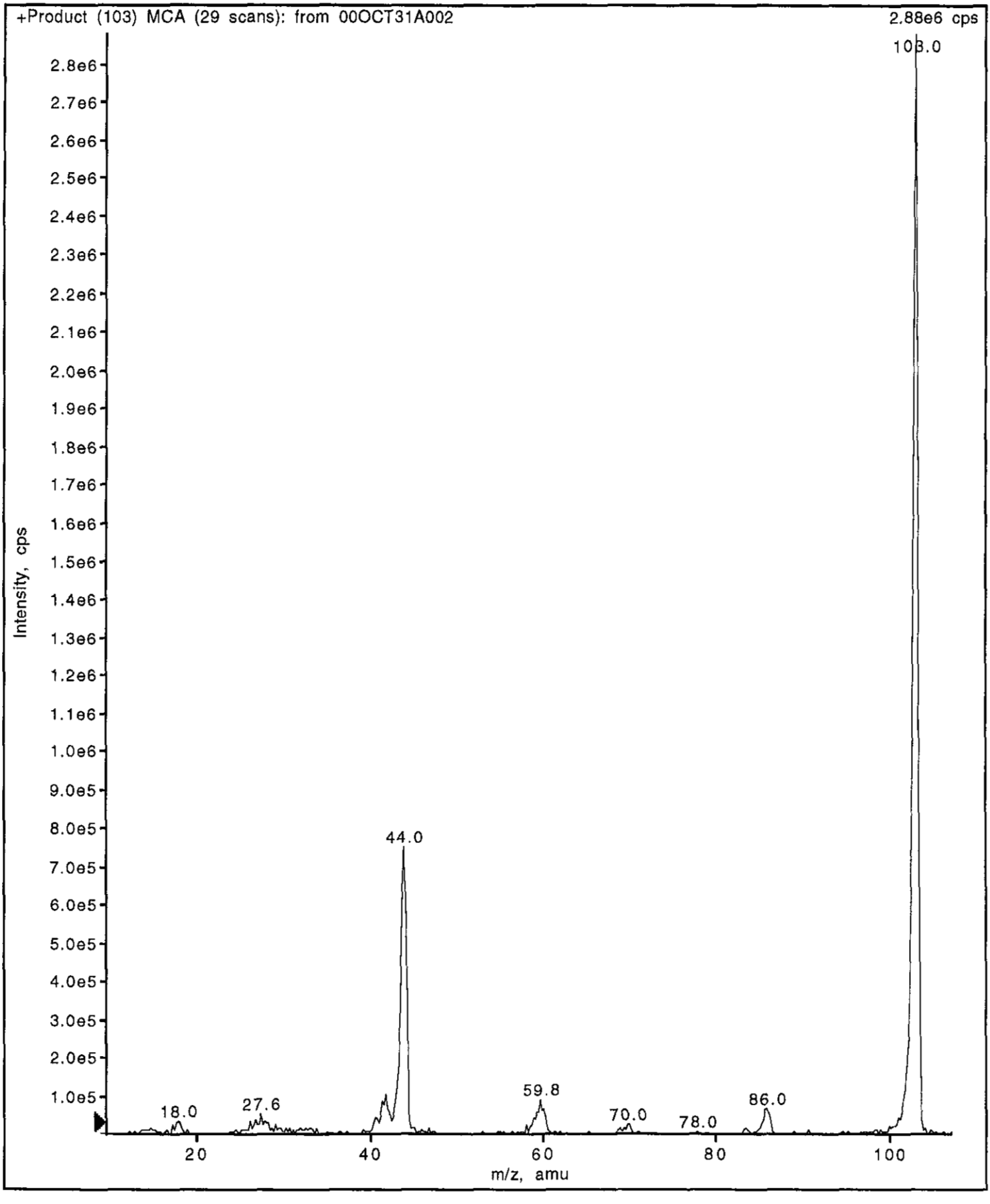
00JUL10A006 (- User: RAP3 - Compound: ACEPHATE)
Period 1, Expt. 1; Mass range: 9.9 to 187.9 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Mon, Jul 10, 2000 at 14:47:56; Exp. Comment: ACEPHATE 182.8 MS/MS Experiment



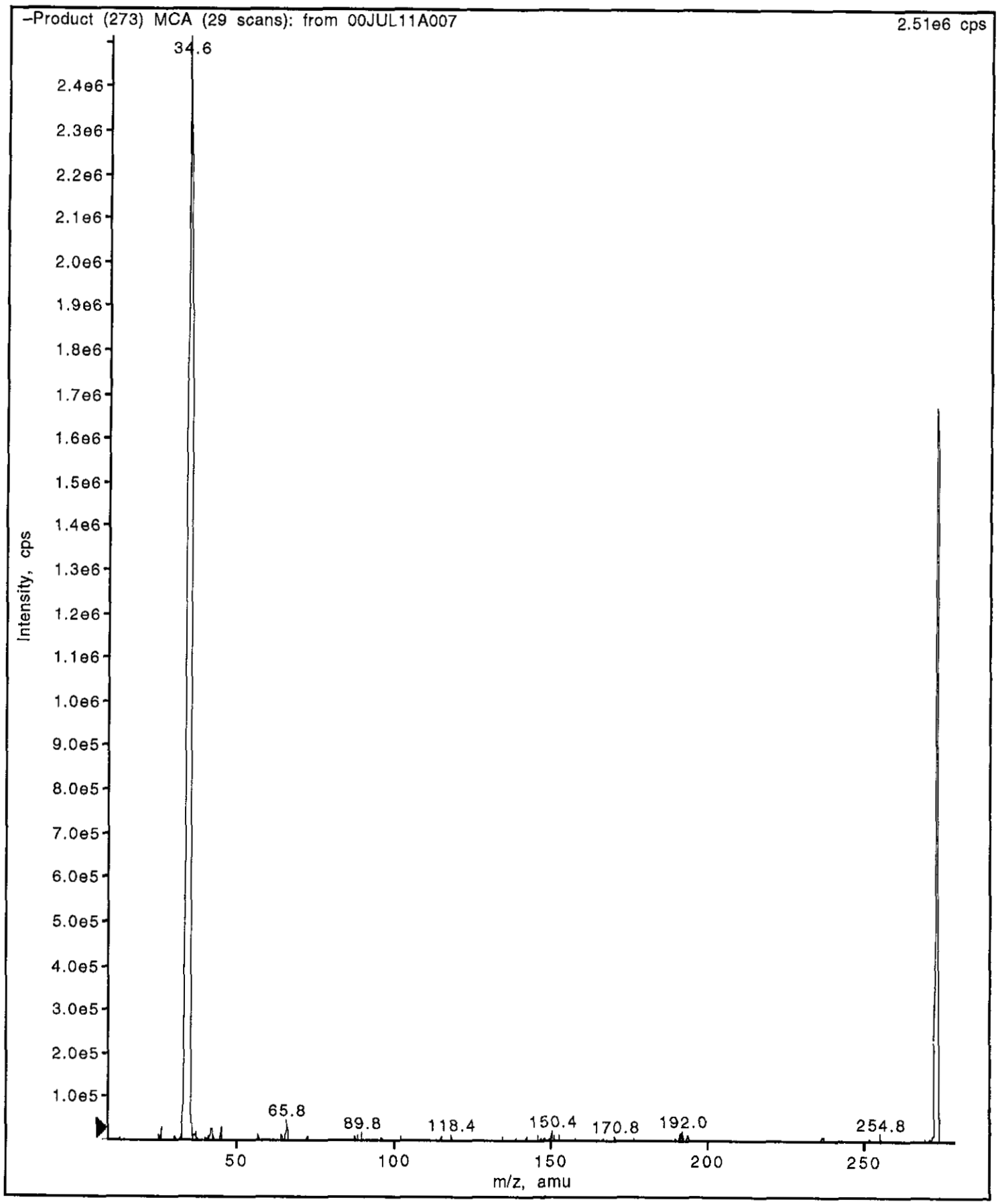
00JUL10A010 (- User: RAP3 - Compound: METHAMIDOPHOS)
Period 1, Expt. 1; Mass range: 9.9 to 146.1 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Mon, Jul 10, 2000 at 15:15:19; Exp. Comment: METHAMIDOPHOS 141.0 MS/MS Experiment



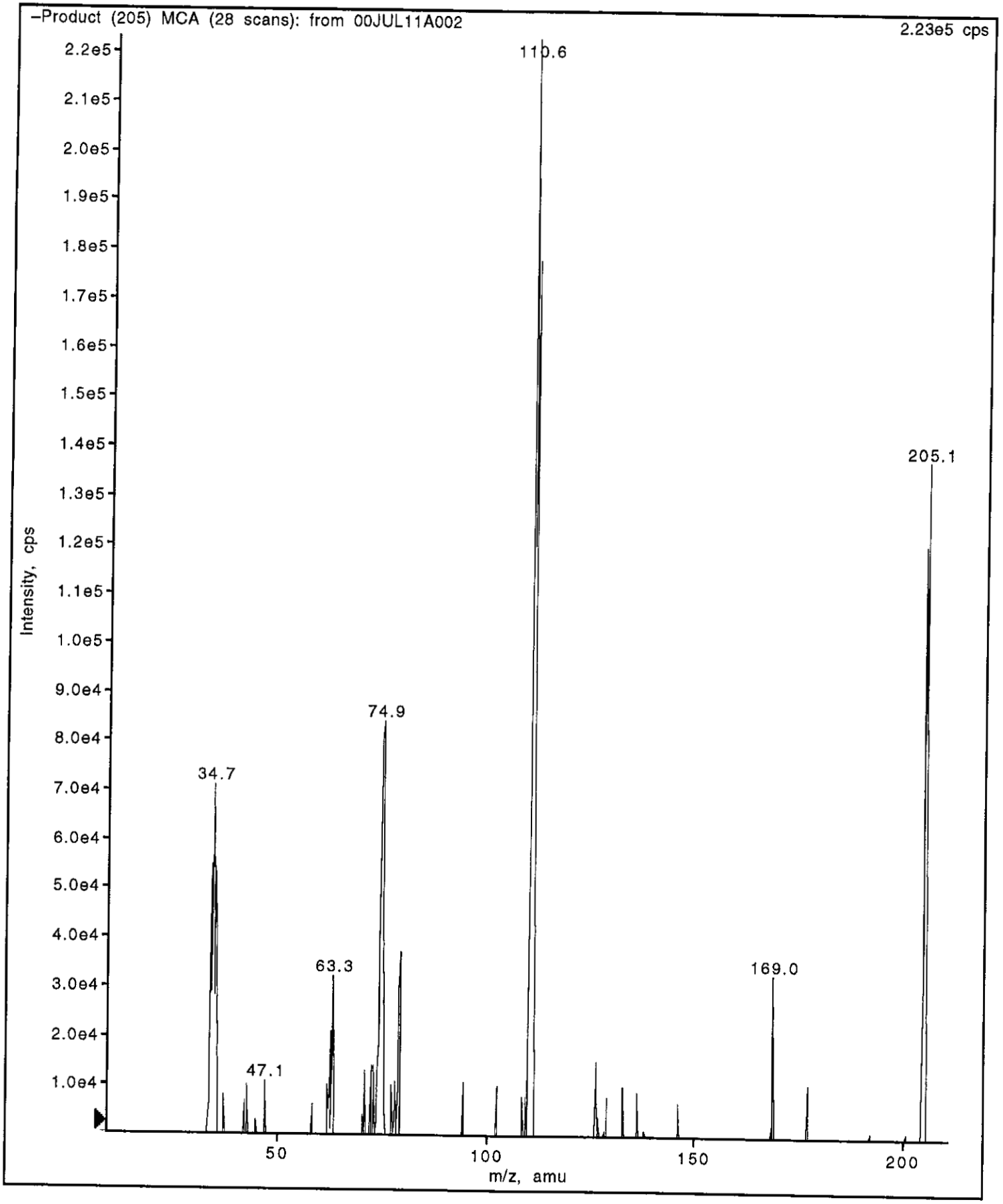
00OCT31A002 (- User: RAP3 - Compound: ETHYLENE THIOUREA)
Period 1, Expt. 1; Mass range: 10.0 to 107.2 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Tue, Oct 31, 2000 at 09:48:41; Exp. Comment: ETHYLENE THIOUREA 102.1 MS/MS Experiment



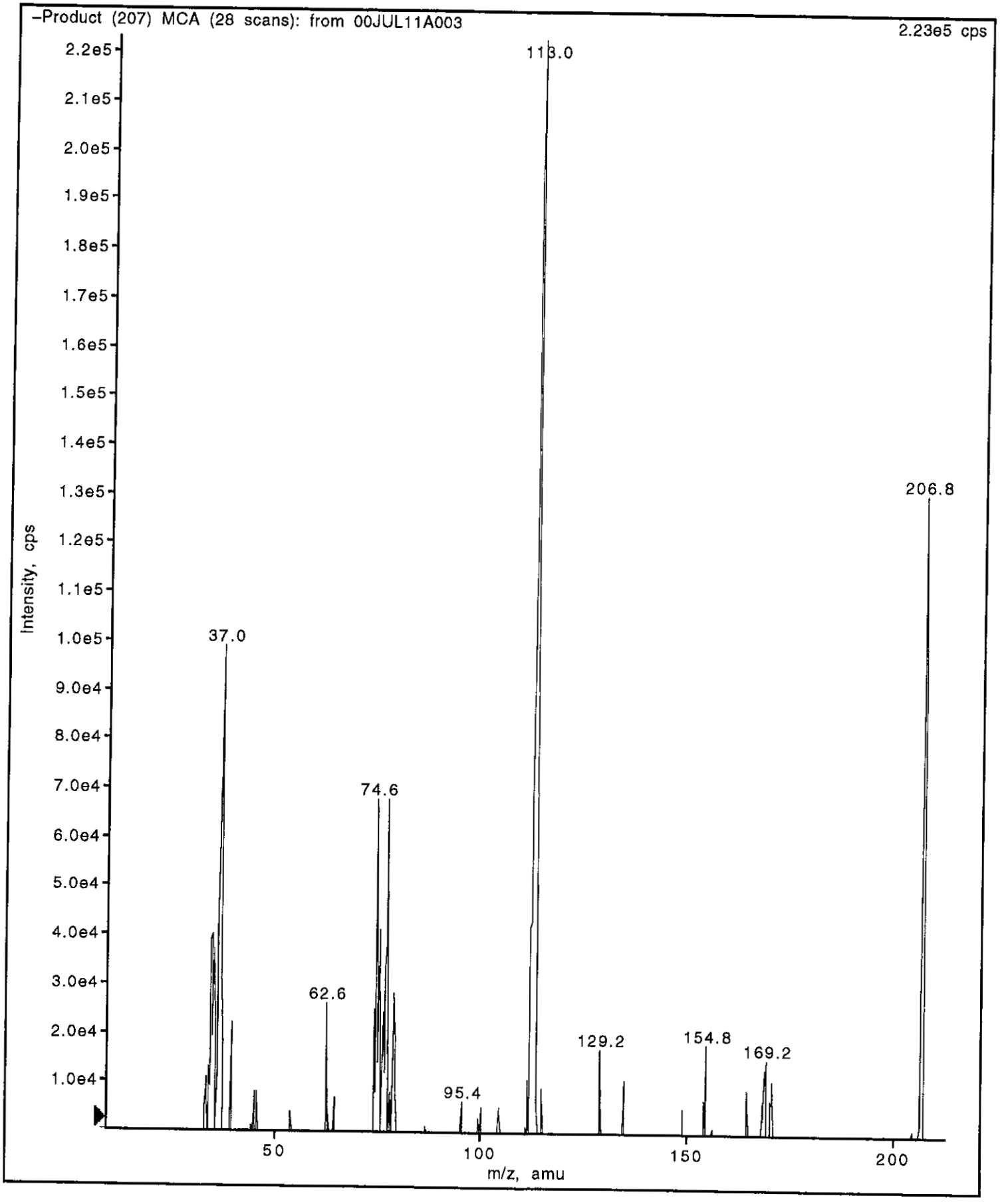
00JUL11A007 (- User: RAP3 - Compound: ANILAZINE)
Period 1, Expt. 1; Mass range: 10.0 to 278.8 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Tue, Jul 11, 2000 at 16:43:10; Exp. Comment: NILAZINE 273.8 MS/MS ExperimentπSt



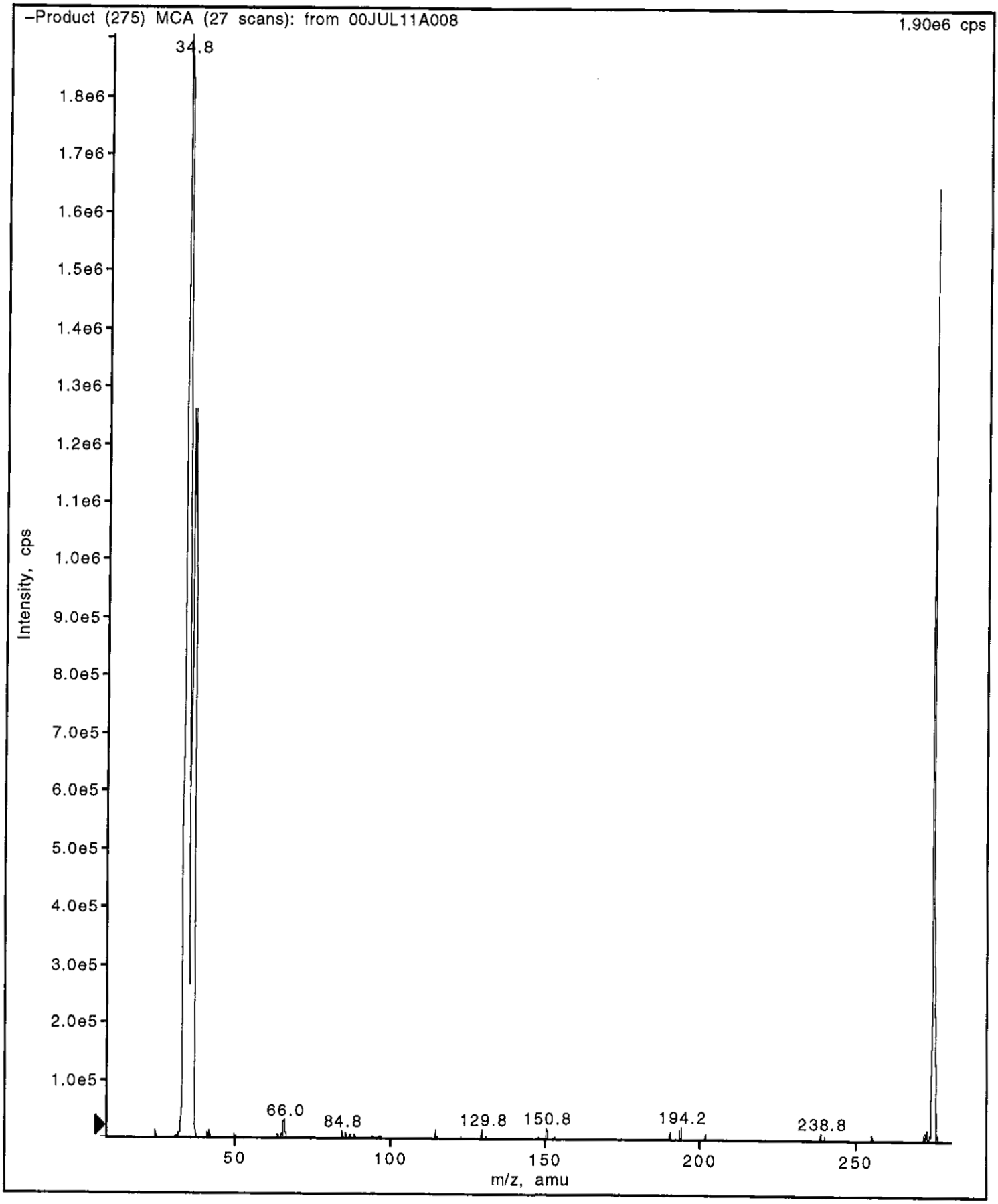
00JUL11A002 (- User: RAP3 - Compound: DICHLORVOS)
Period 1, Expt. 1; Mass range: 9.9 to 210.9 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Tue, Jul 11, 2000 at 15:49:04; Exp. Comment: DICHLORVOS 205.8 MS/MS Experiment



00JUL11A003 (- User: RAP3 - Compound: DICHLORVOS)
Period 1, Expt. 1; Mass range: 10.0 to 212.8 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Tue, Jul 11, 2000 at 15:52:09; Exp. Comment: DICHLORVOS 207.7 MS/MS Experiment



00JUL11A008 (- User: RAP3 - Compound: ANILAZINE)
Period 1, Expt. 1; Mass range: 10.0 to 280.8 by 0.2 amu; Dwell: 1.0 ms; Pause: 2.0 ms
Acq. Time: Tue, Jul 11, 2000 at 16:46:11; Exp. Comment: NILAZINE 275.7 MS/MS ExperimentπSt



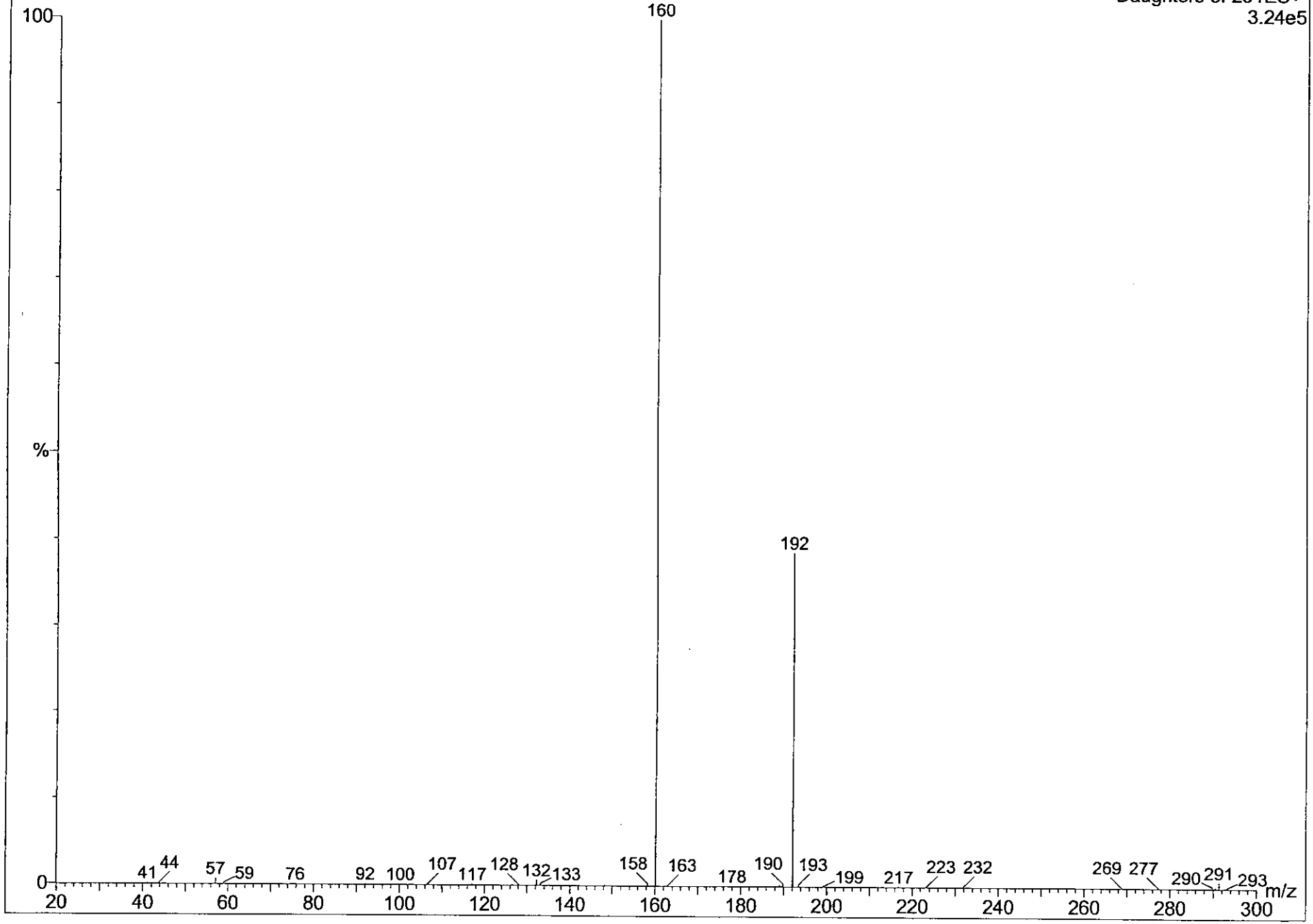
Appendix B

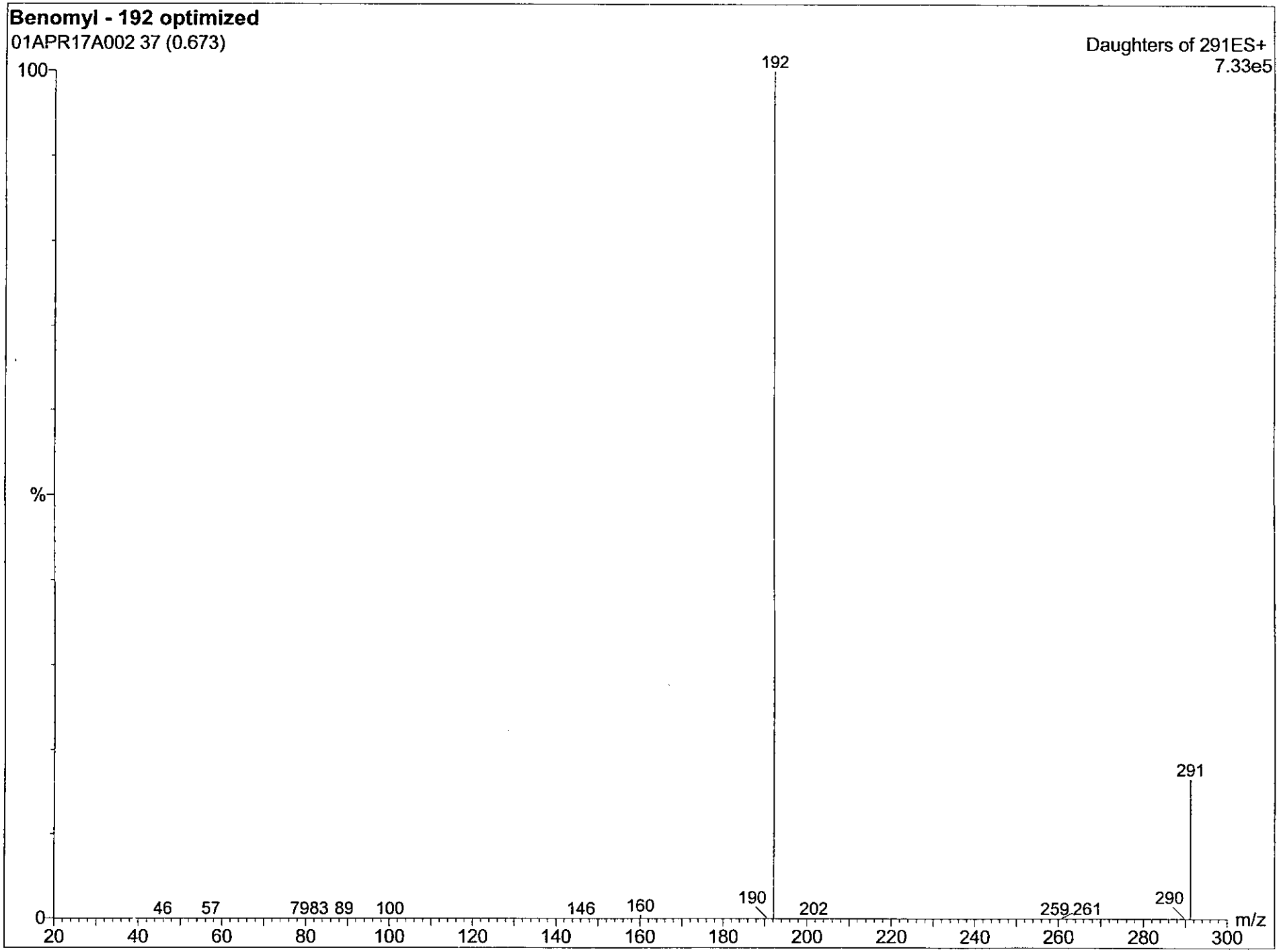
MS/MS Daughter Ion Spectra of Target Analytes
Quattro LC

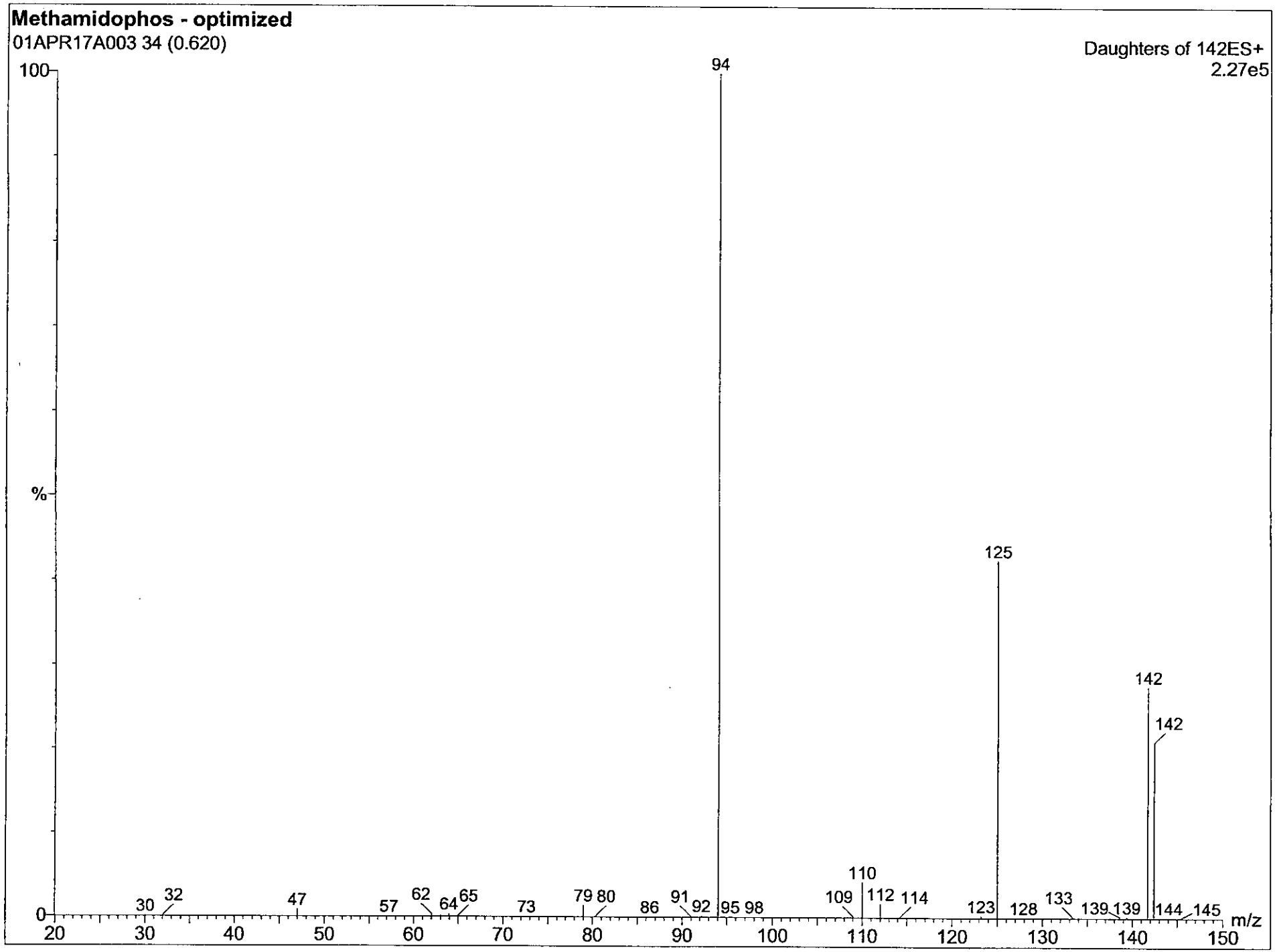
Benomyl - 160 optimized

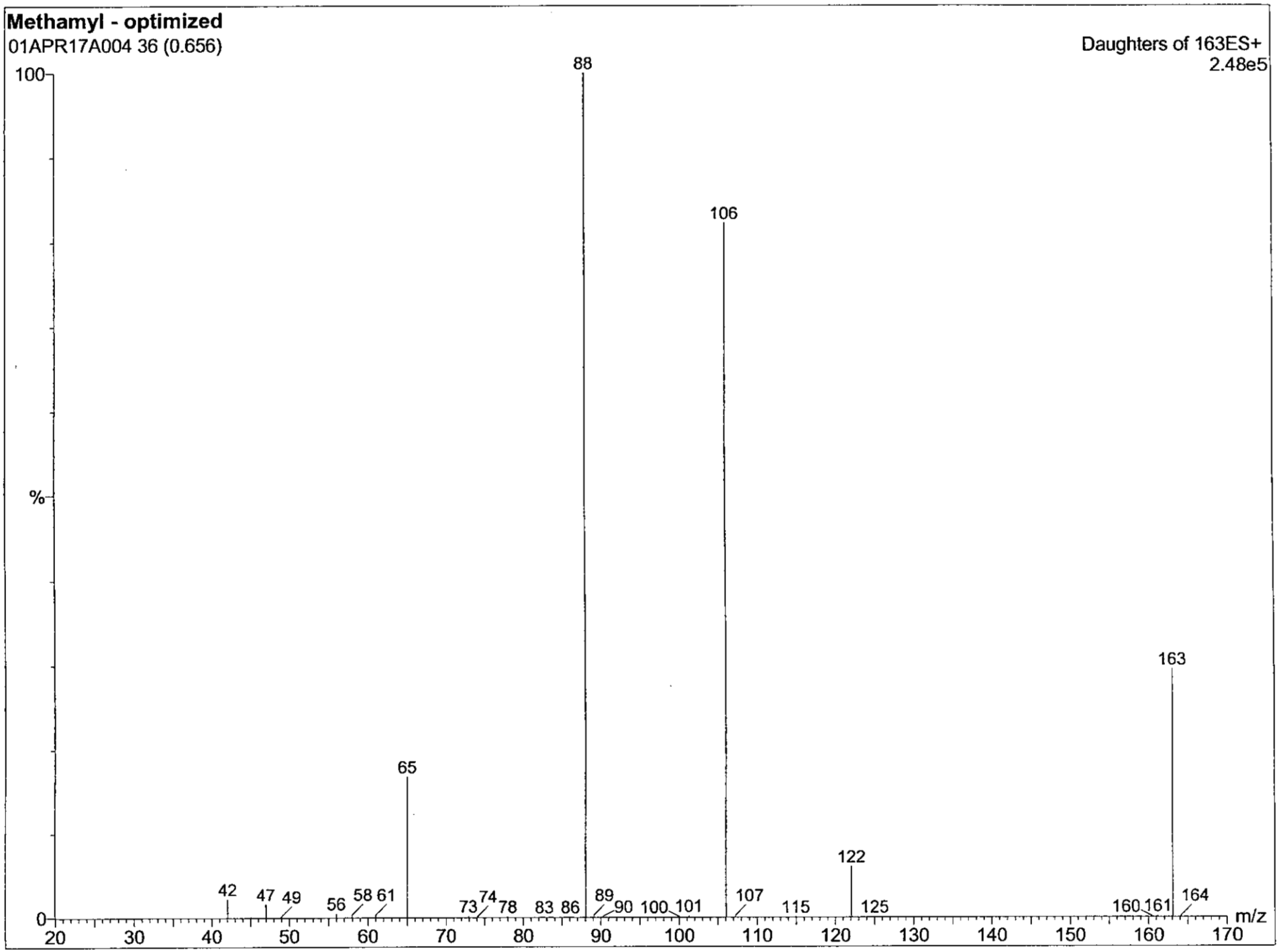
01APR17A001 1 (0.043)

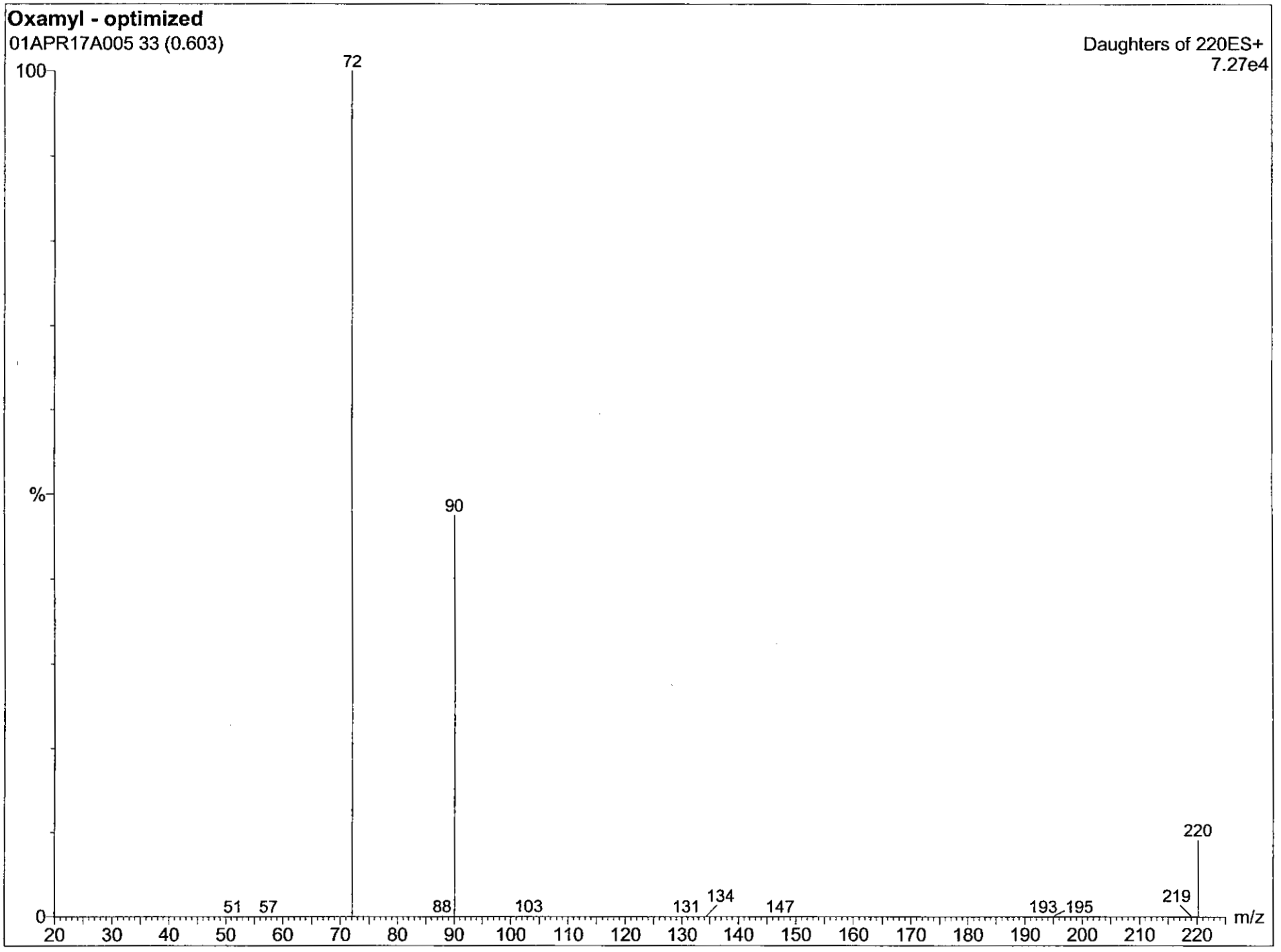
Daughters of 291ES+
3.24e5

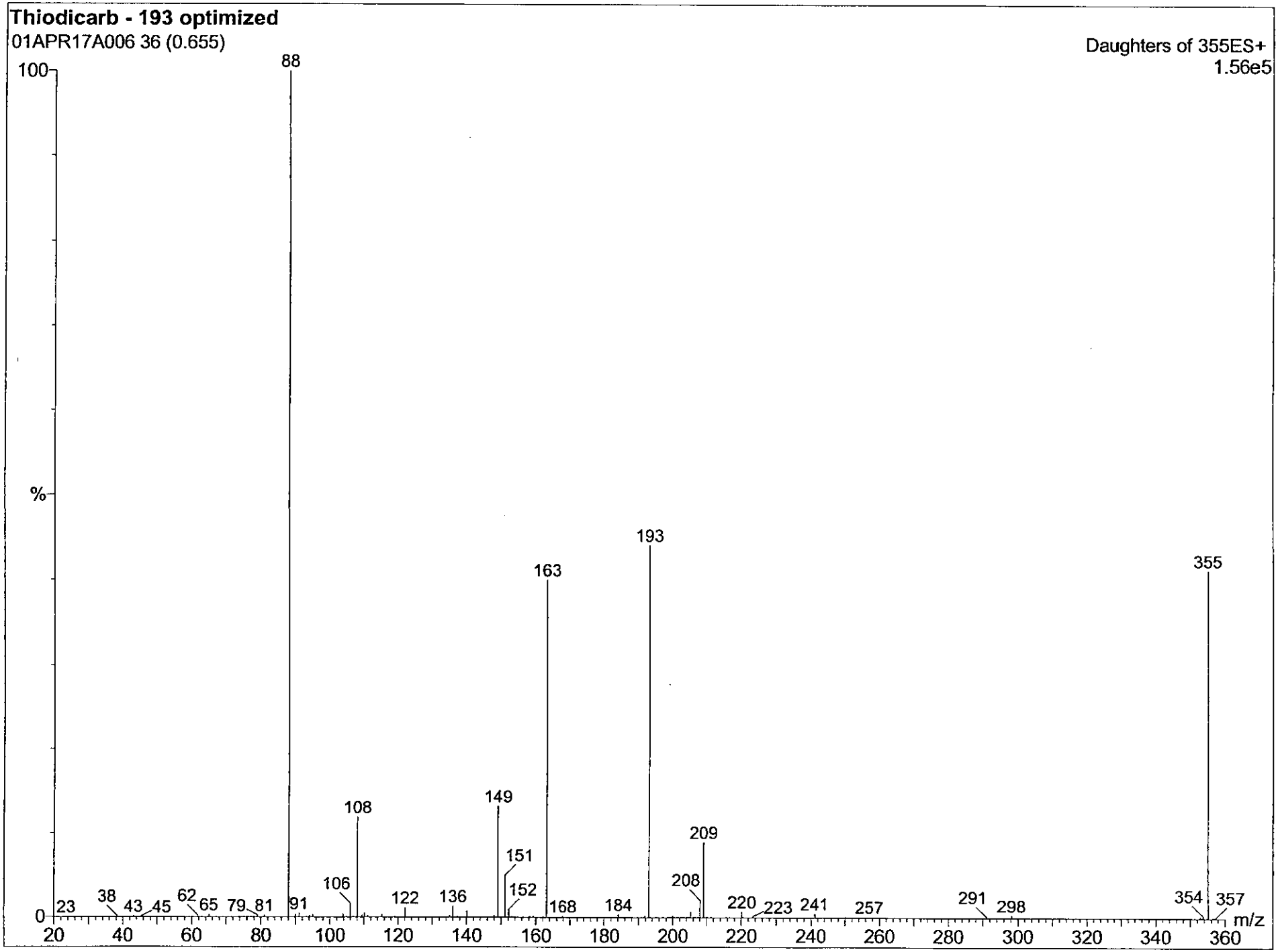


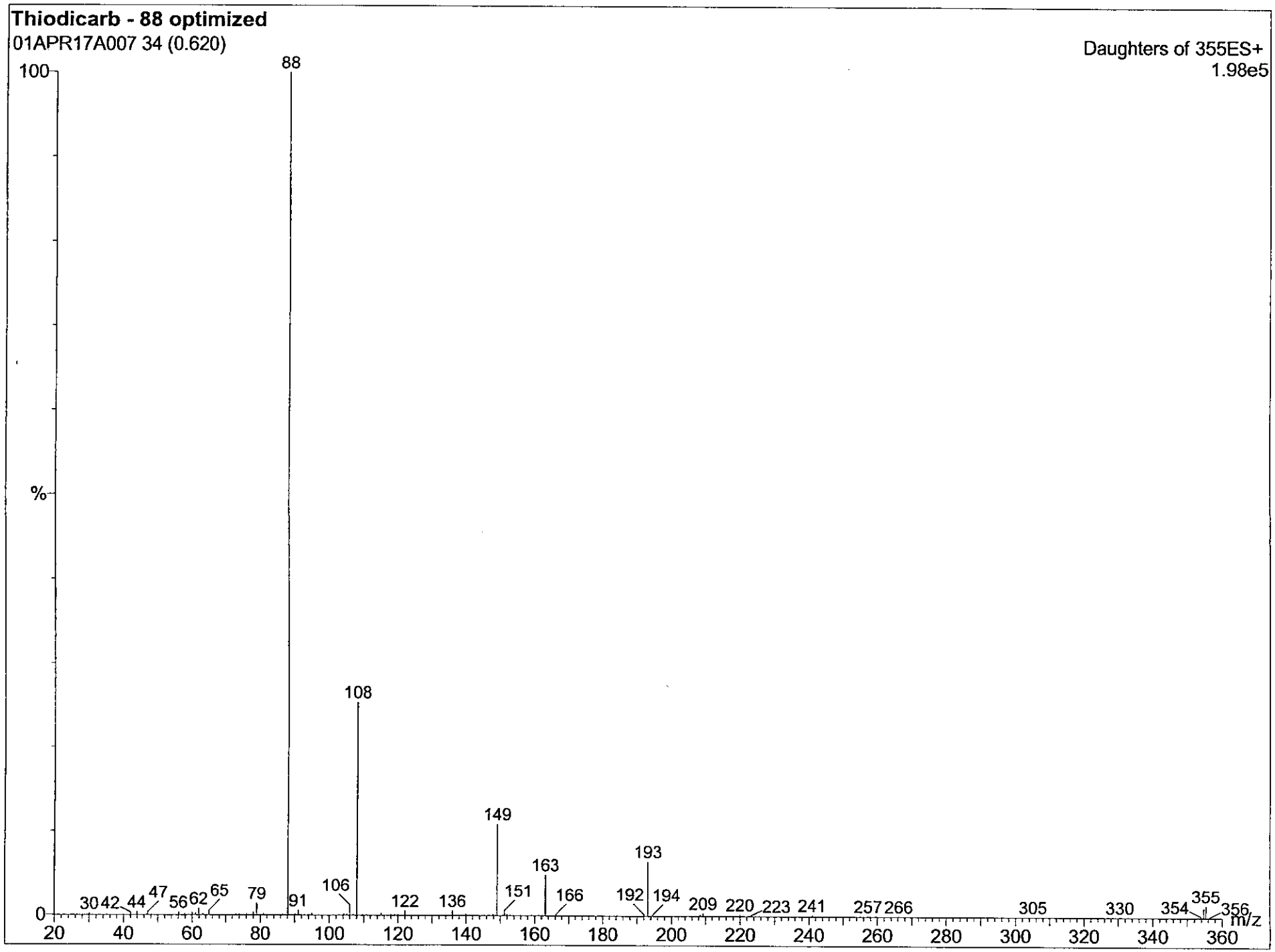

Benomyl - 192 optimized
01APR17A002 37 (0.673)
Daughters of 291ES+
7.33e5
100
%
0
192
291
190
290
46
57
79
83
89
100
146
160
202
259
261
m/z
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300


Methamidophos - optimized
01APR17A003 34 (0.620)
Daughters of 142ES+
2.27e5
100
%
0
94
125
142
142
110
30
32
47
57
62
64
65
73
79
80
86
91
92
95
98
109
112
114
123
128
133
139
139
144
145
m/z
20
30
40
50
60
70
80
90
100
110
120
130
140
150


Methamyl - optimized
01APR17A004 36 (0.656)
Daughters of 163ES+
2.48e5
100
%
0
88
106
163
65
122
42
47
49
56
58
61
73
74
78
83
86
89
90
100
101
107
115
125
160
161
164
m/z
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170


Oxamyl - optimized
01APR17A005 33 (0.603)
Daughters of 220ES+
7.27e4
100
%
0
72
90
220
219
51
57
88
103
131
134
147
193
195
m/z
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

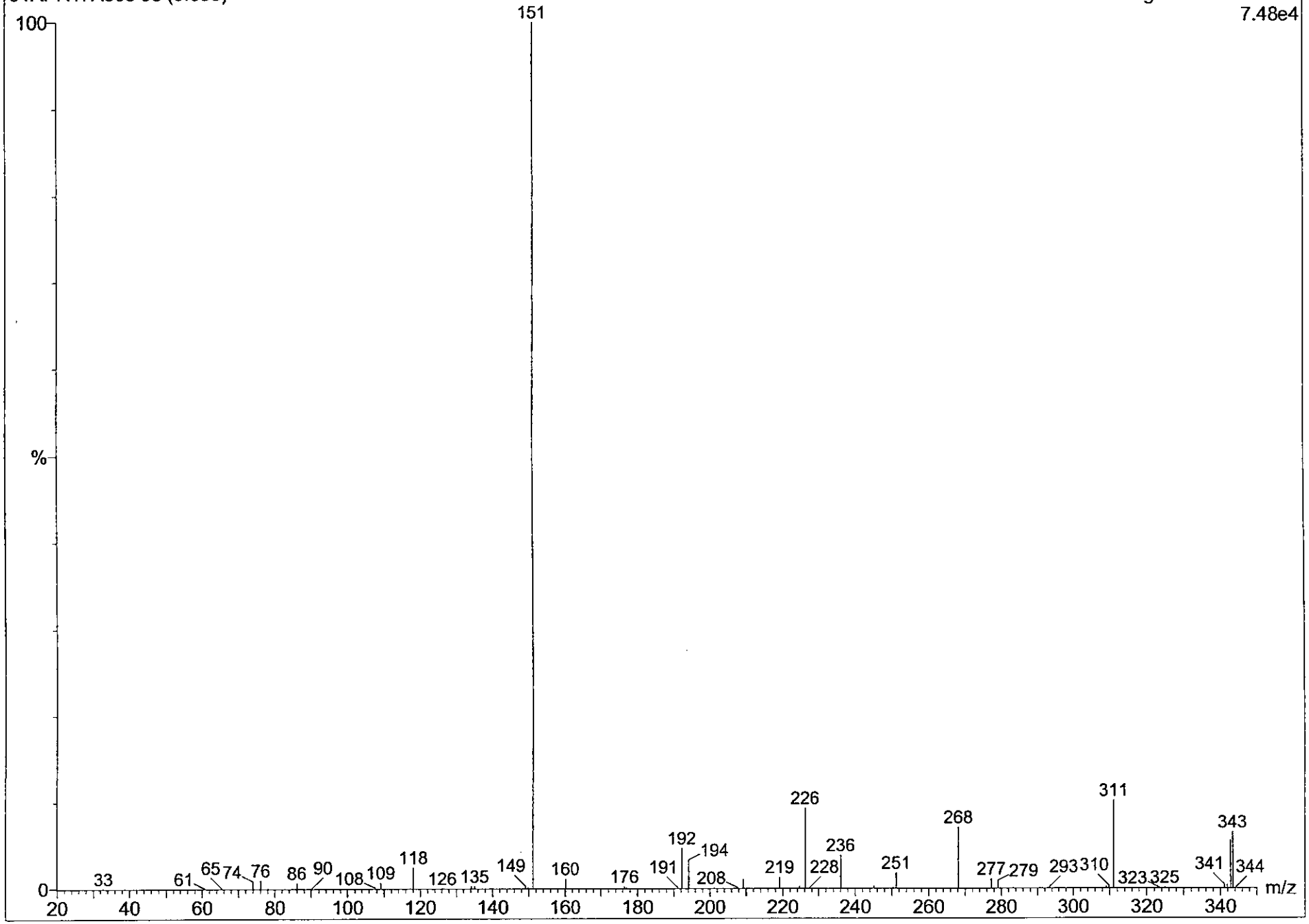

Thiodicarb - 193 optimized
01APR17A006 36 (0.655)
Daughters of 355ES+
1.56e5
100
%
0
88
193
163
355
149
108
209
151
106
208
152
23
38
43
45
62
65
79
81
91
122
136
168
184
220
223
241
257
291
298
354
357
m/z
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360

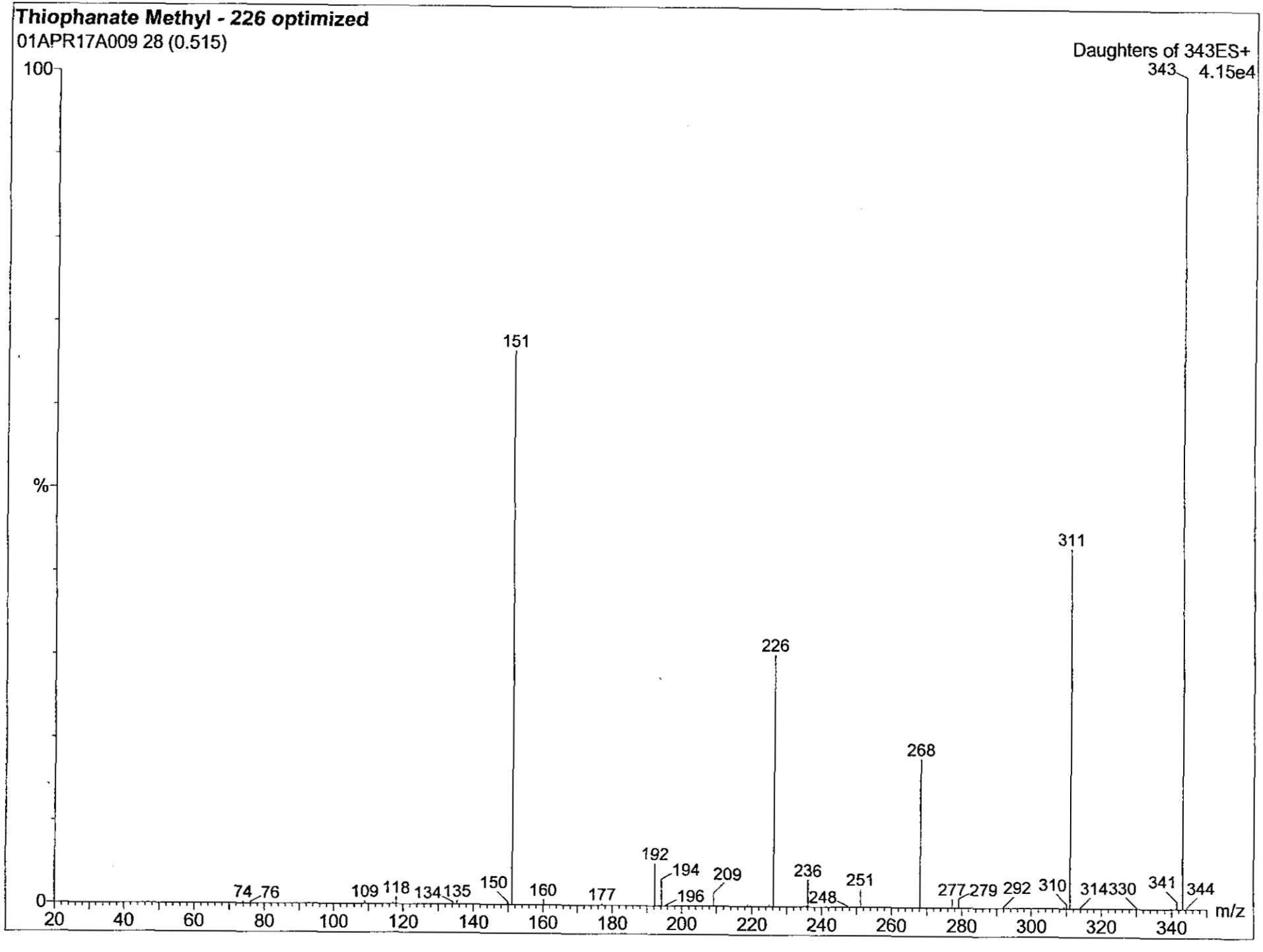

Thiodicarb - 88 optimized
01APR17A007 34 (0.620)
Daughters of 355ES+
1.98e5
100
%
0
88
108
149
163
193
106
151
166
192
194
30 42 44 47 56 62 65 79 91 122 136 209 220 223 241 257 266 305 330 354 355 356
m/z
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360

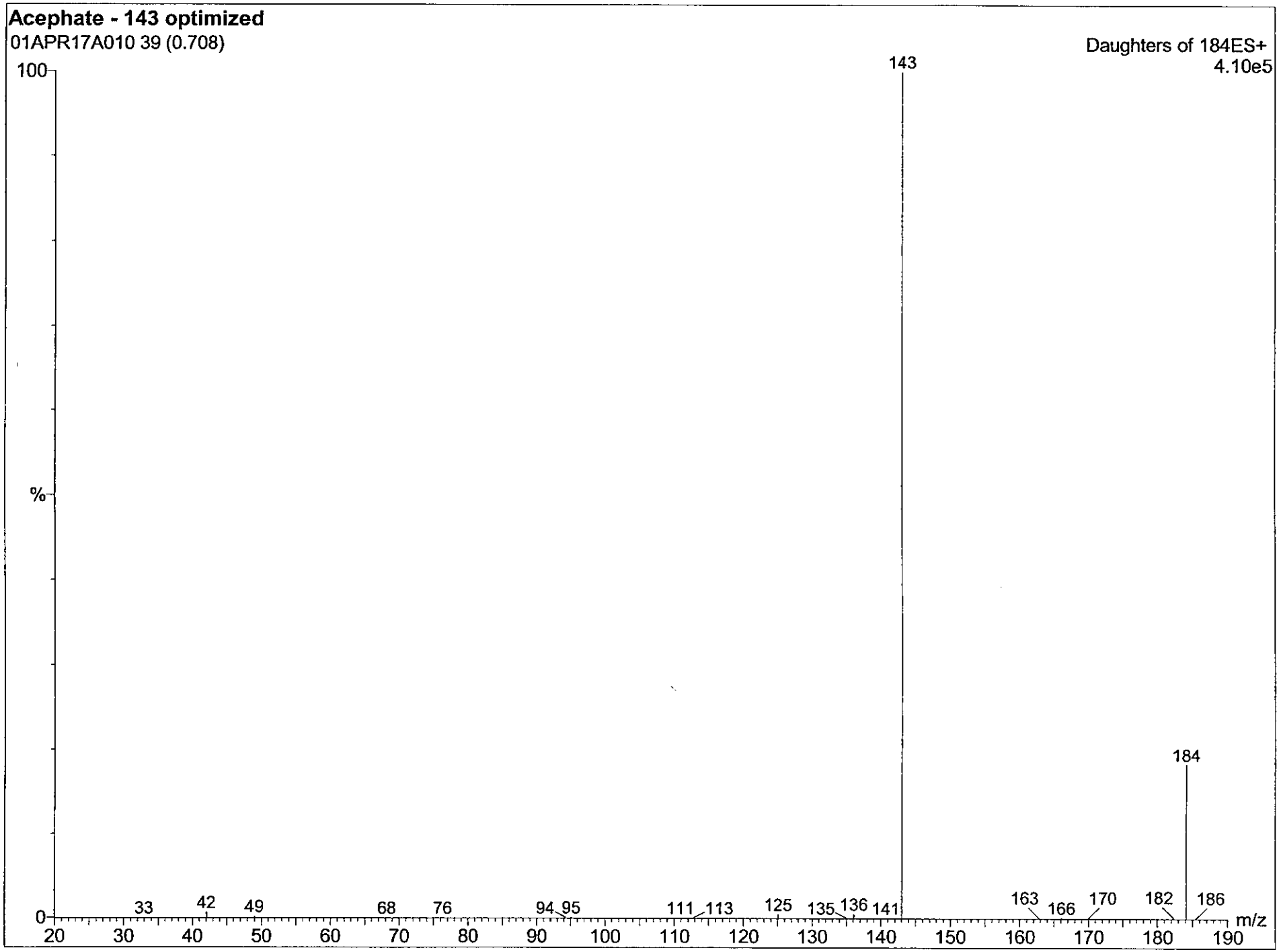
Thiophanate Methyl - 151 optimized

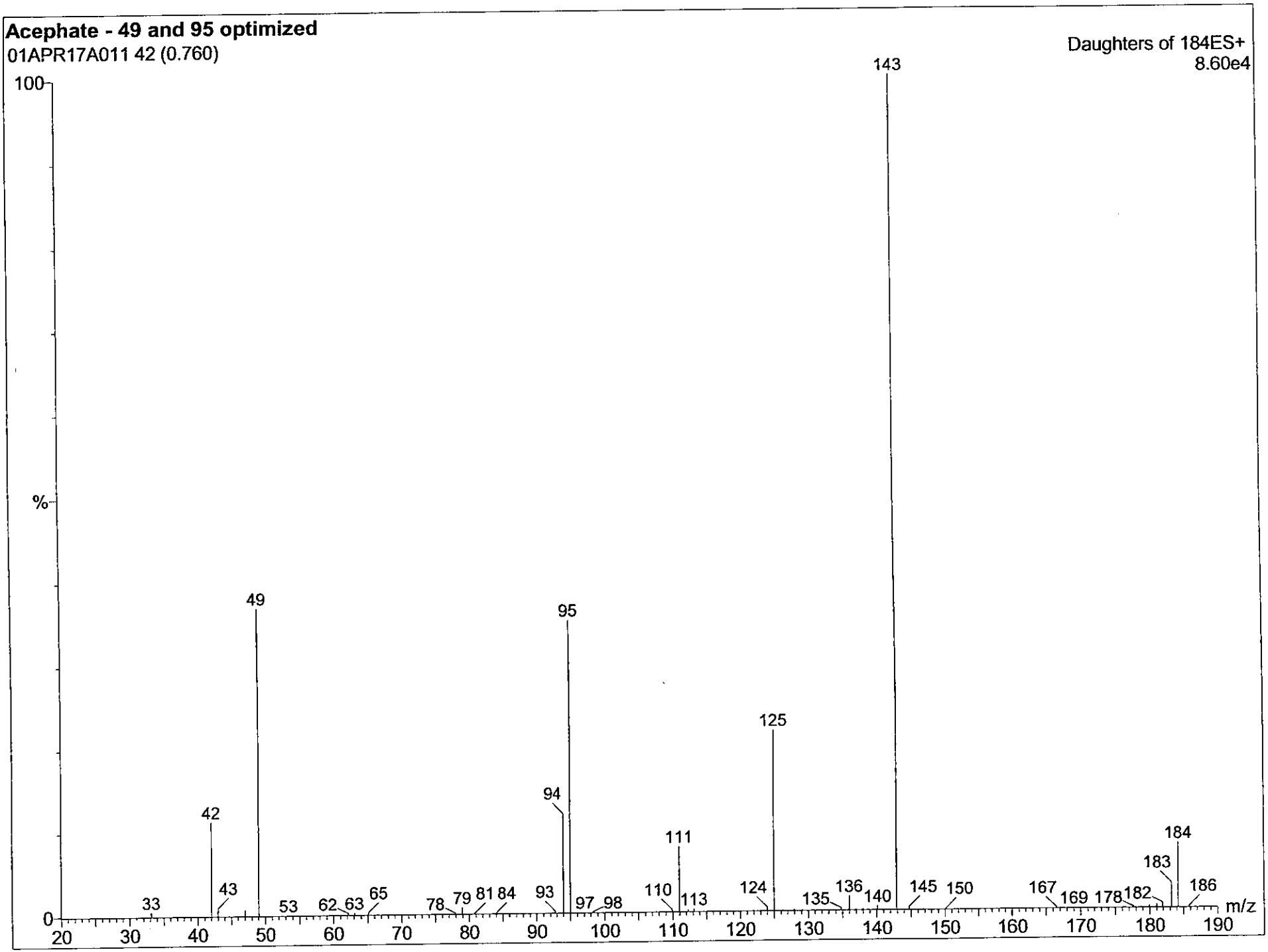
01APR17A008 35 (0.638)

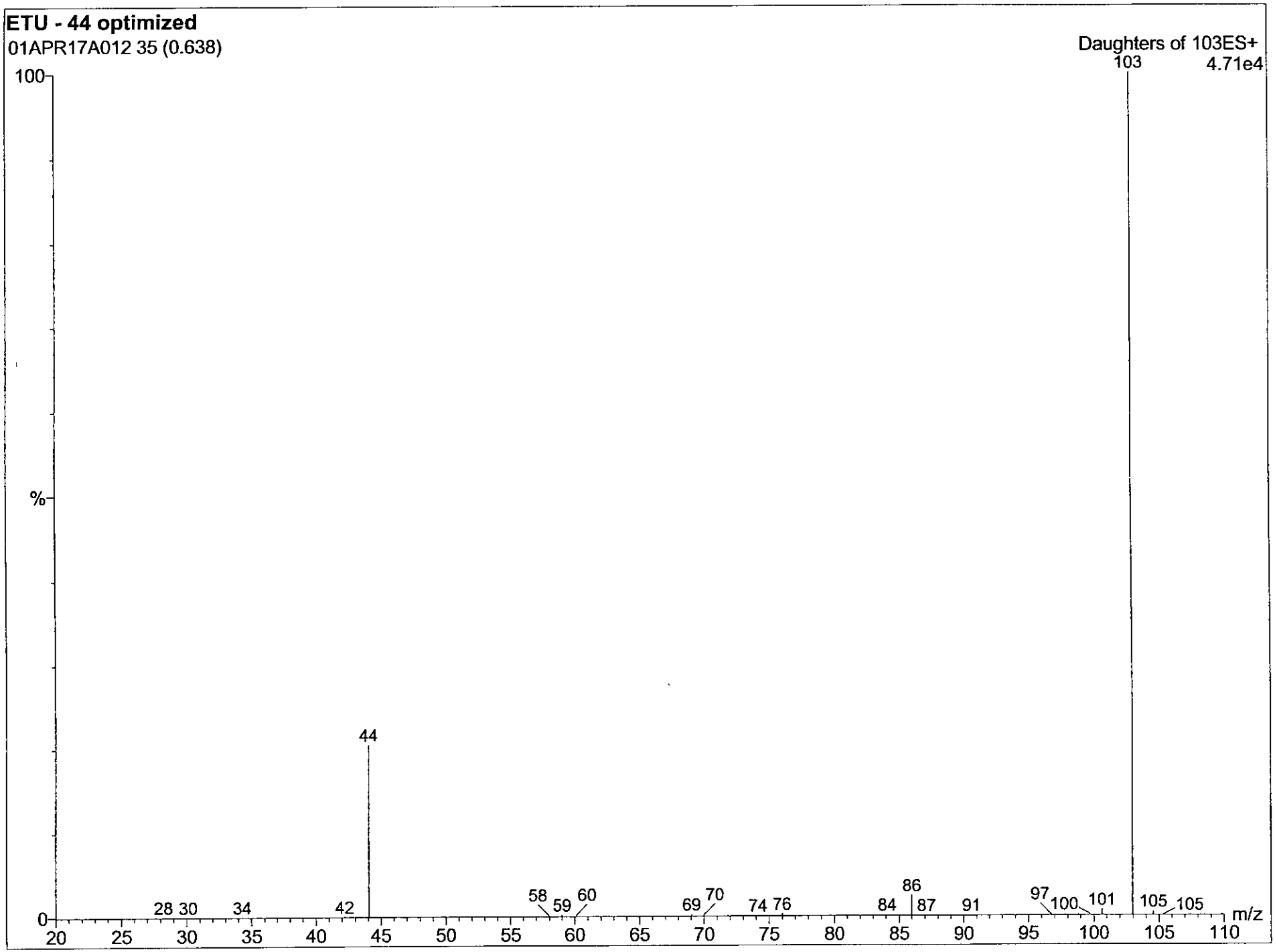
Daughters of 343ES+
7.48e4

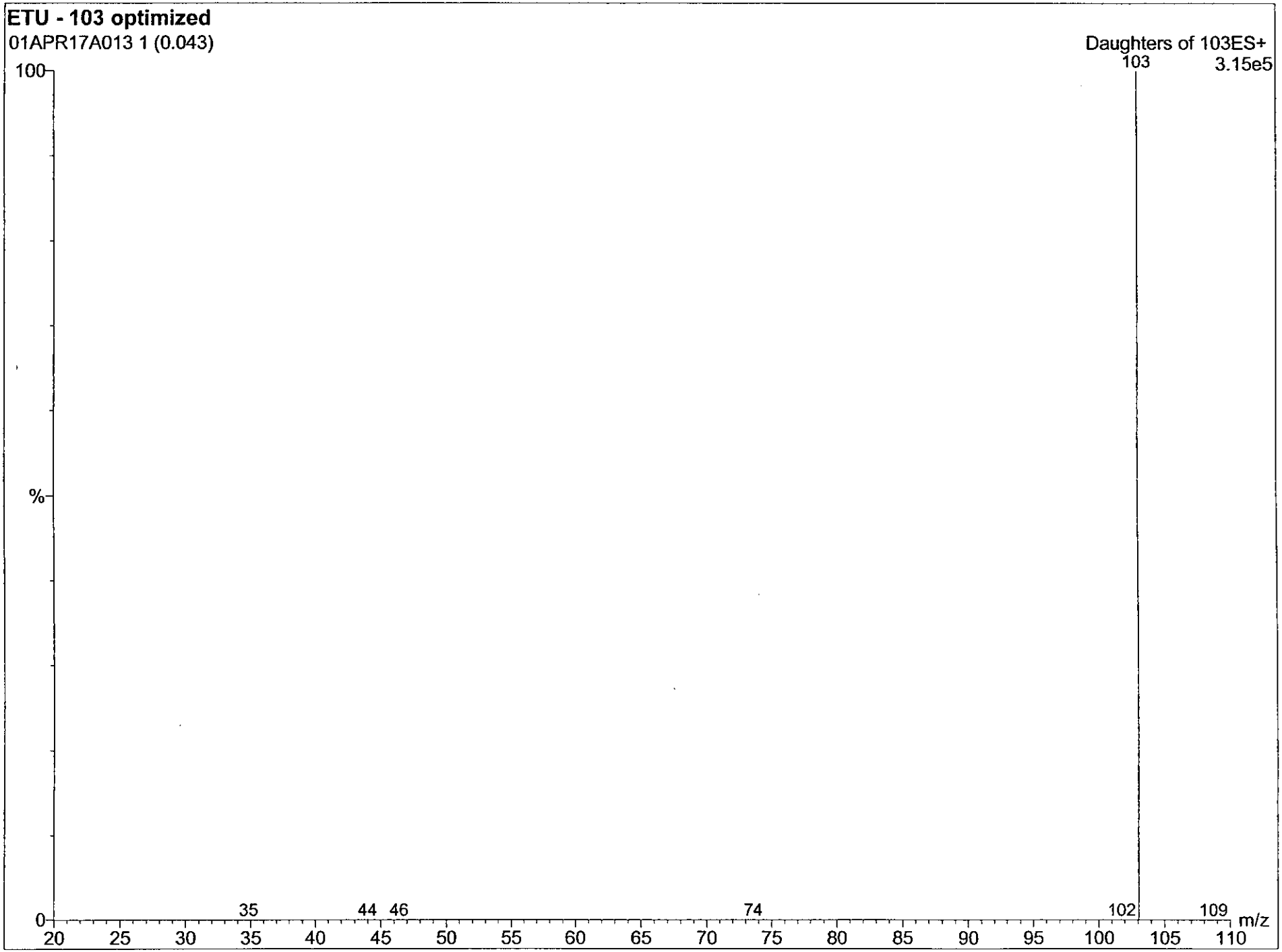


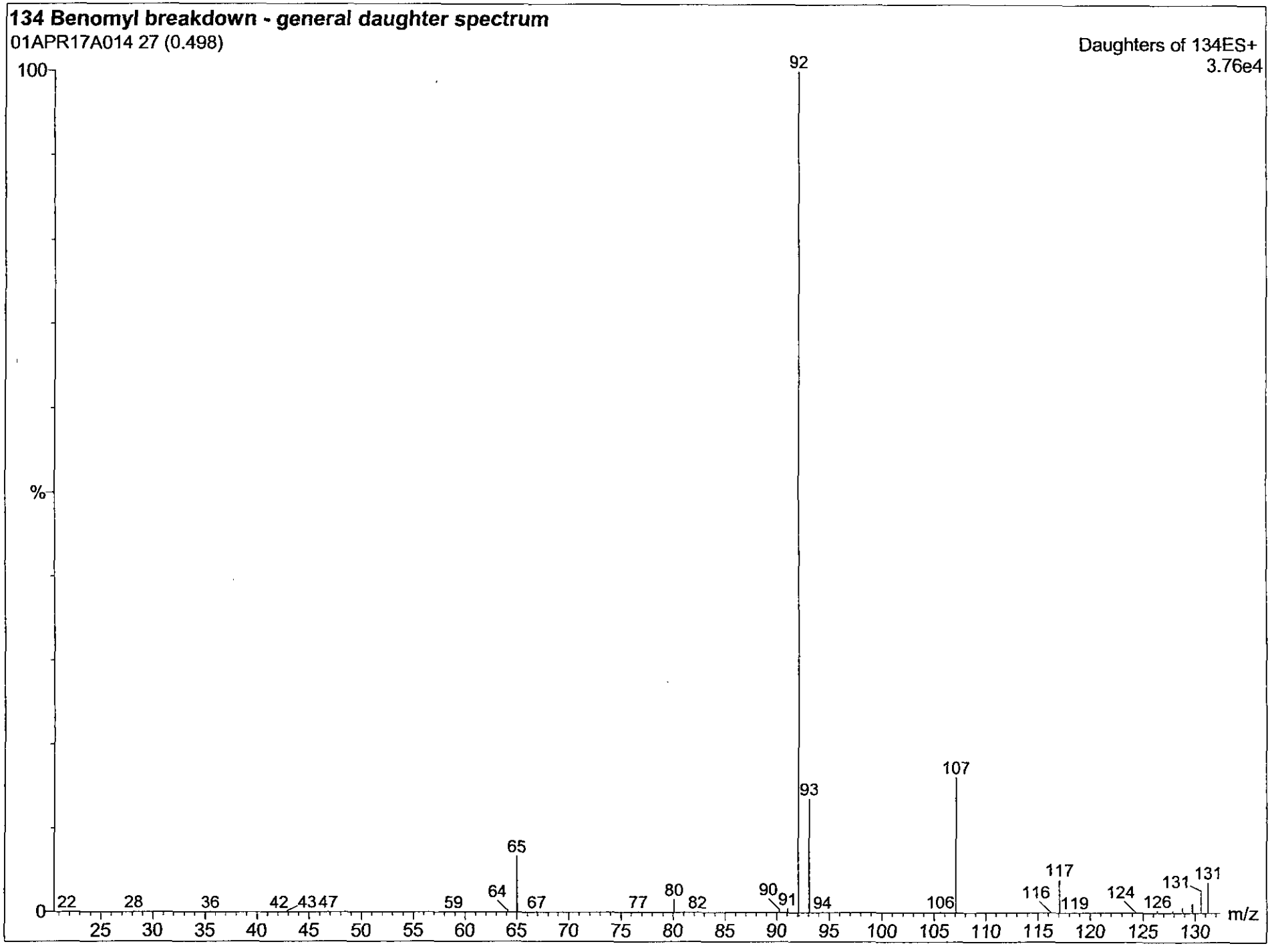

Thiophanate Methyl - 226 optimized
01APR17A009 28 (0.515)
Daughters of 343ES+
343
4.15e4
100
%
0
151
311
226
268
192
194
209
236
251
74
76
109
118
134
135
150
160
177
196
248
277
279
292
310
314
330
341
344
m/z
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340

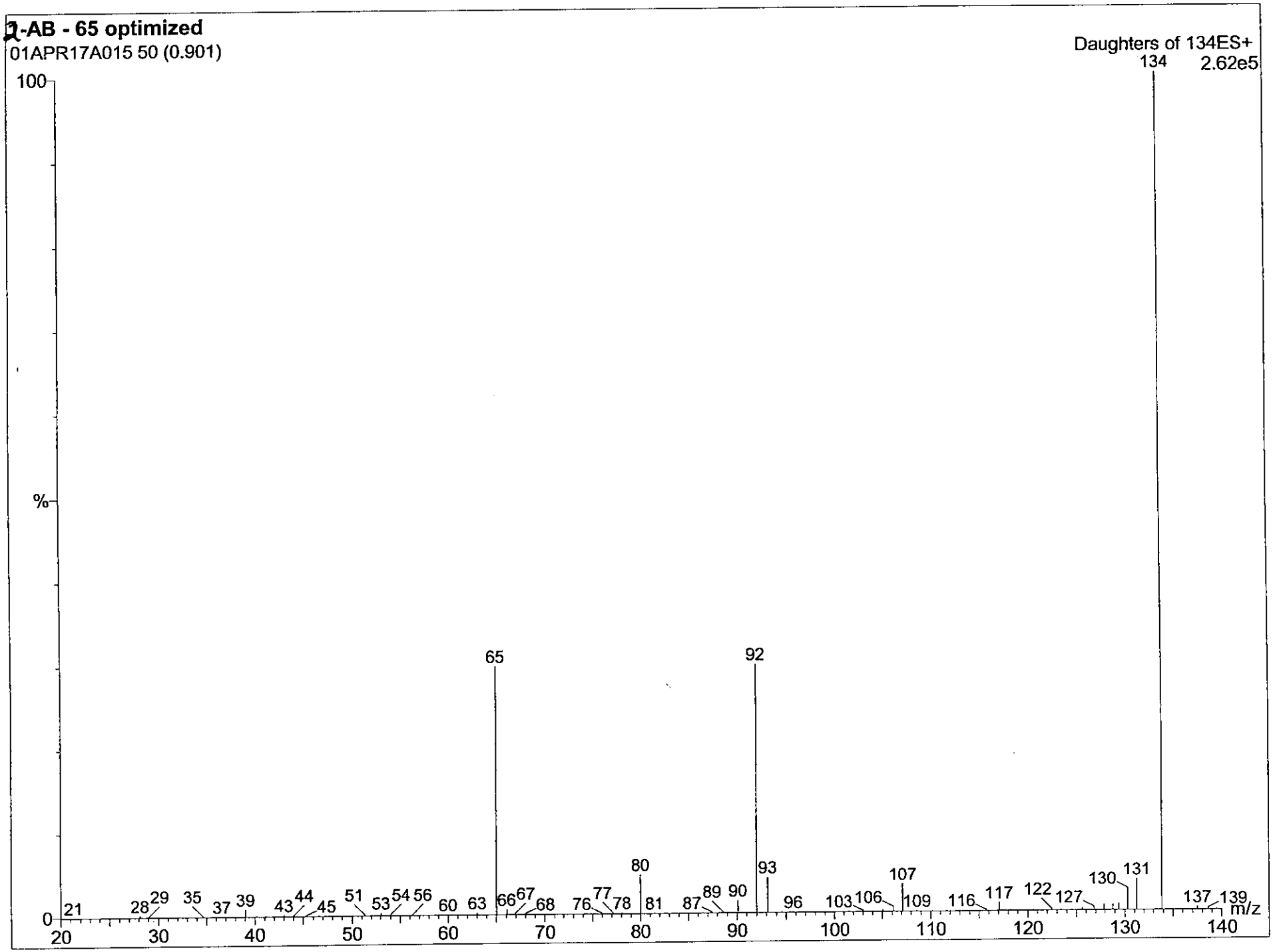

Acephate - 143 optimized
01APR17A010 39 (0.708)
Daughters of 184ES+
4.10e5
100
%
0
143
184
33
42
49
68
76
94
95
111
113
125
135
136
141
163
166
170
182
186
m/z
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

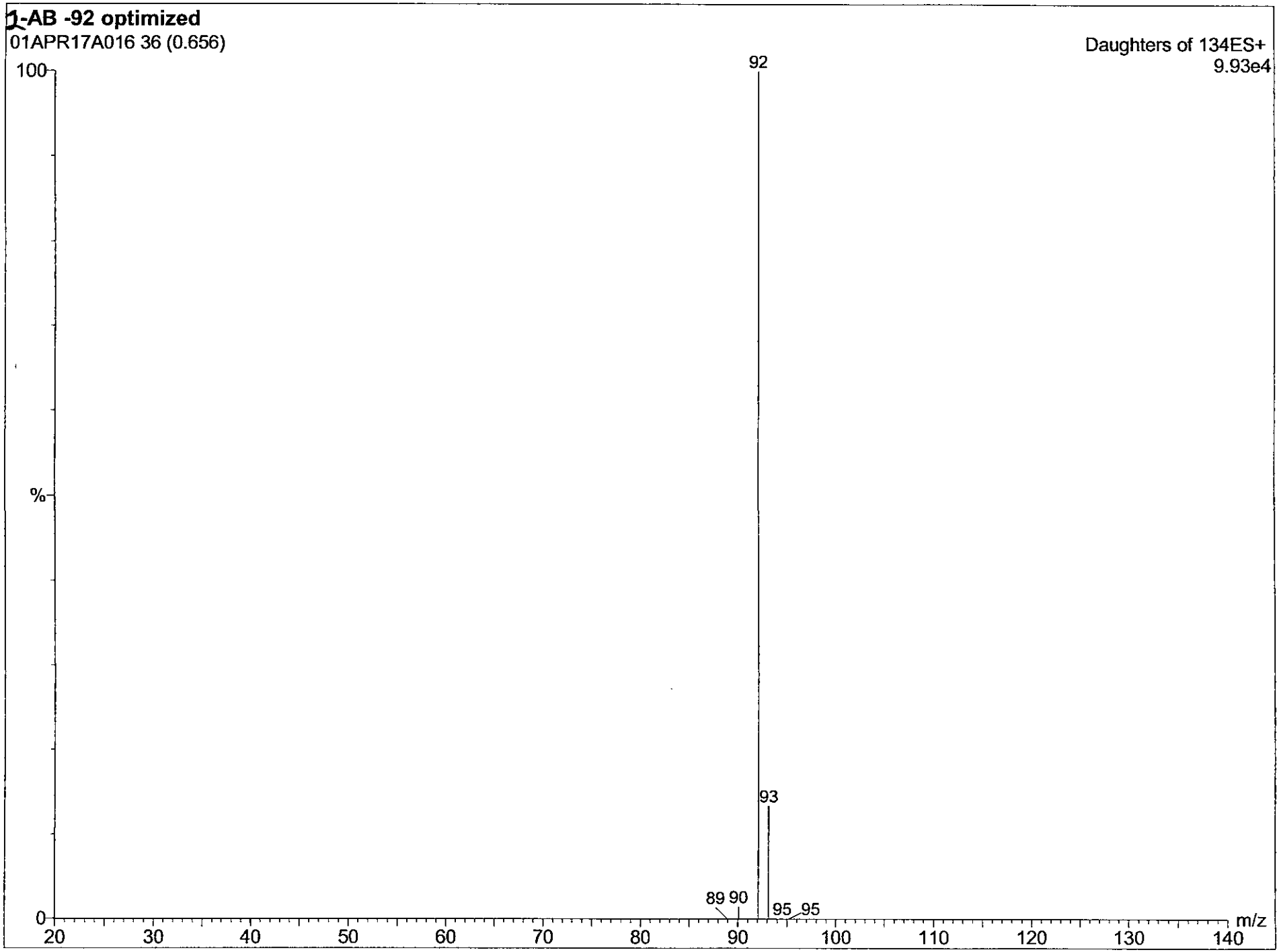

Acephate - 49 and 95 optimized
01APR17A011 42 (0.760)
Daughters of 184ES+
8.60e4
100
%
0
143
49
95
125
94
42
111
184
183
186
43
33
53
62
63
65
78
79
81
84
93
97
98
110
113
124
135
136
140
145
150
167
169
178
182
m/z
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

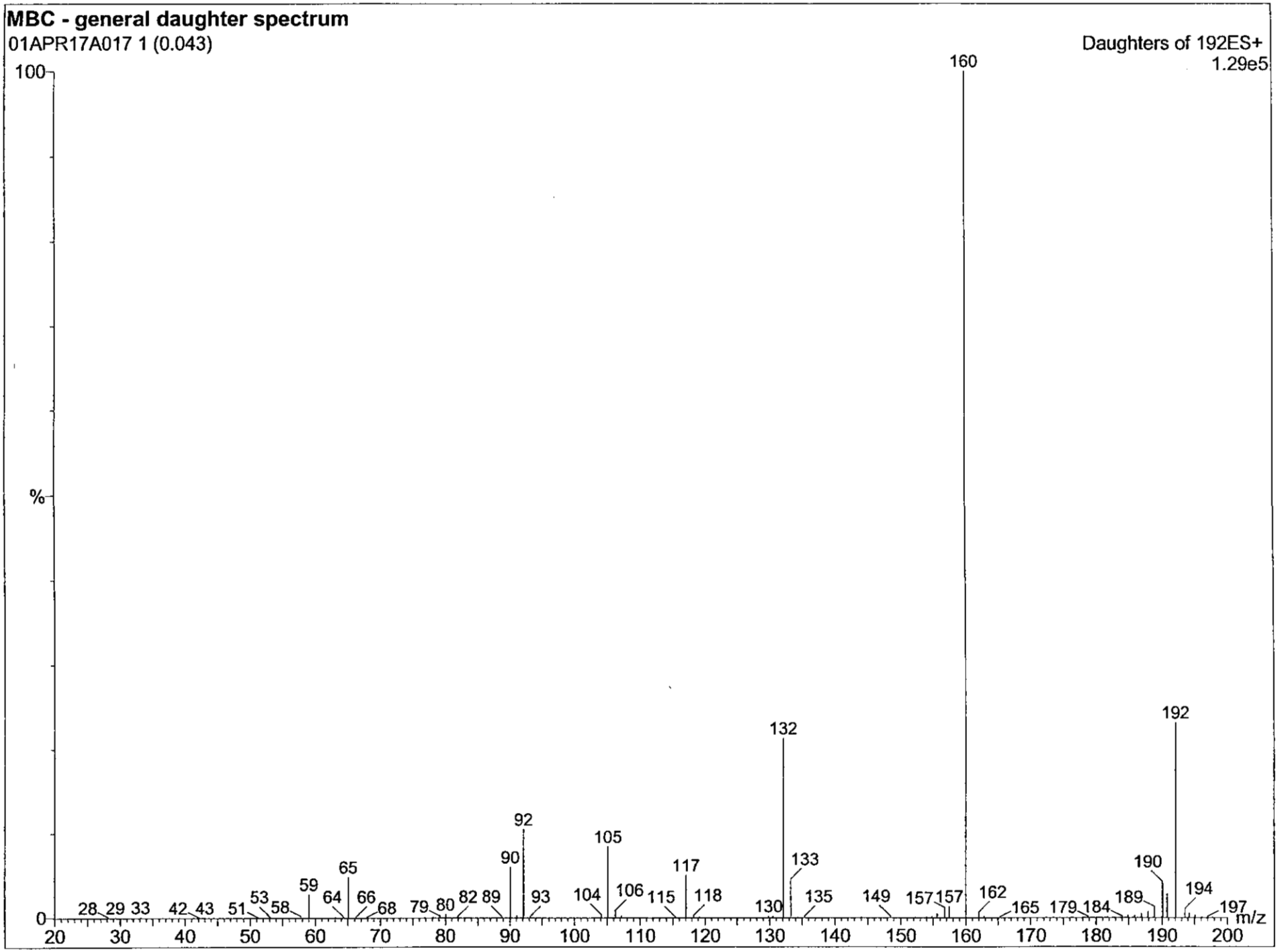

ETU - 44 optimized
01APR17A012 35 (0.638)
Daughters of 103ES+
103
4.71e4
100
%
0
44
28 30
34
42
58
59
60
69
70
74 76
84
86
87
91
97
100
101
105
105
m/z
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110

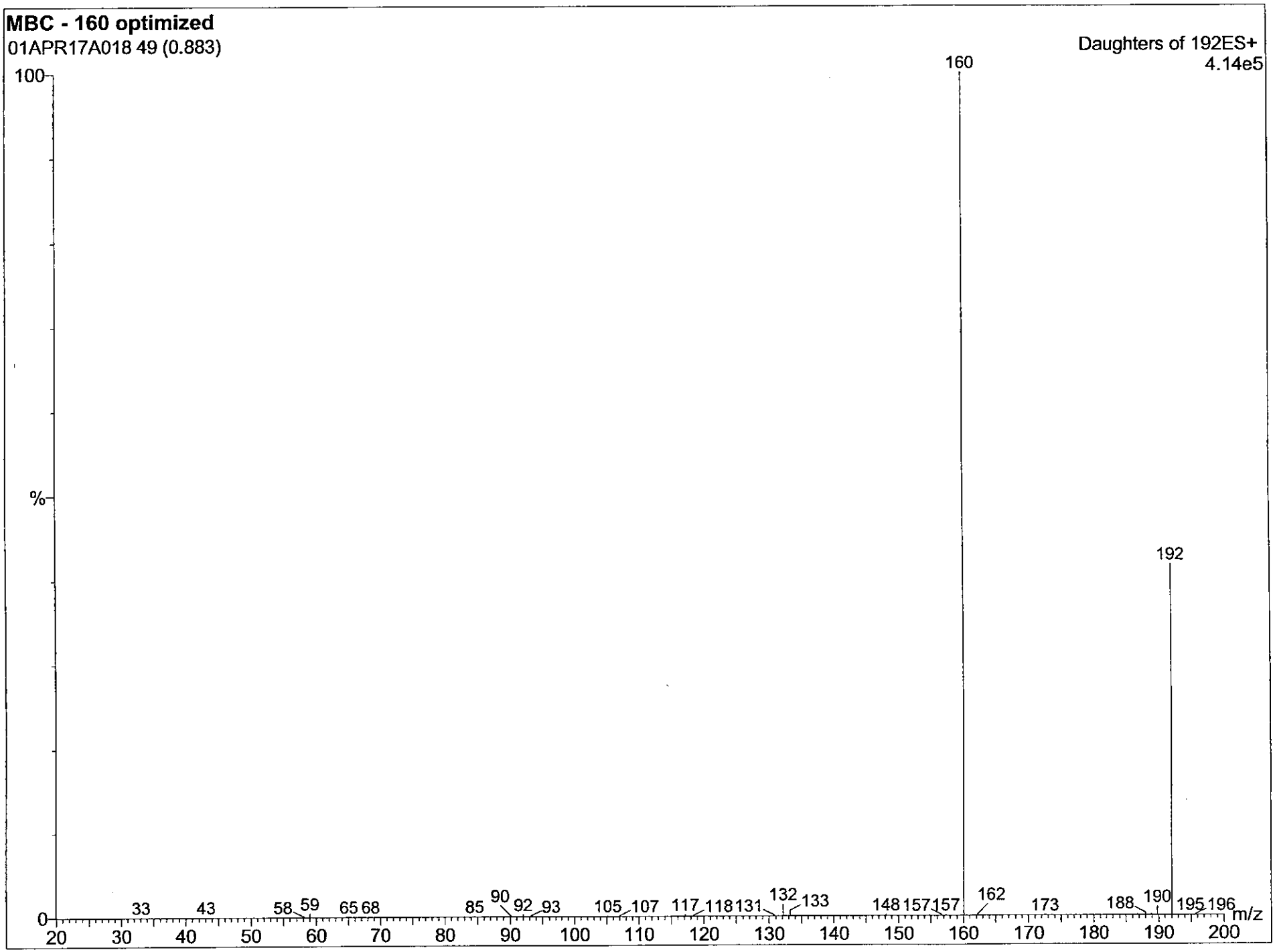

ETU - 103 optimized
01APR17A013 1 (0.043)
Daughters of 103ES+
103
3.15e5
100
%
0
35
44
46
74
102
109
m/z
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110

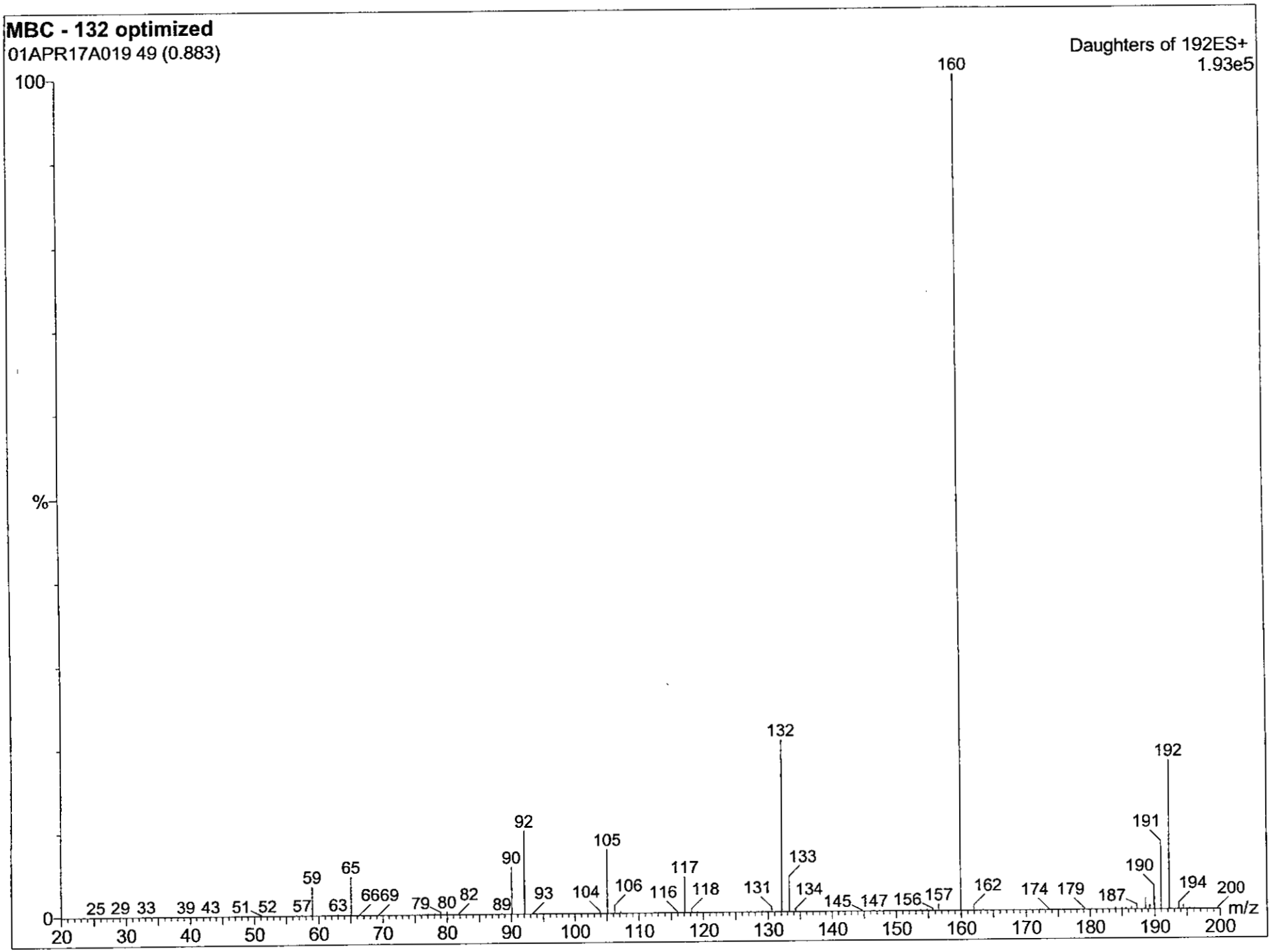

134 Benomyl breakdown - general daughter spectrum
01APR17A014 27 (0.498)
Daughters of 134ES+
3.76e4
100
%
0
92
93
107
65
117
131
131
22
28
36
42
43
47
59
64
67
77
80
82
90
91
94
106
116
119
124
126
m/z
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130


2-AB - 65 optimized
01APR17A015 50 (0.901)
Daughters of 134ES+
134 2.62e5
100
%
0
65
92
80
93
107
131
130
m/z
20
30
40
50
60
70
80
90
100
110
120
130
140


1-AB -92 optimized
01APR17A016 36 (0.656)
Daughters of 134ES+
9.93e4
100
%
0
92
93
89 90
95 95
m/z
20 30 40 50 60 70 80 90 100 110 120 130 140

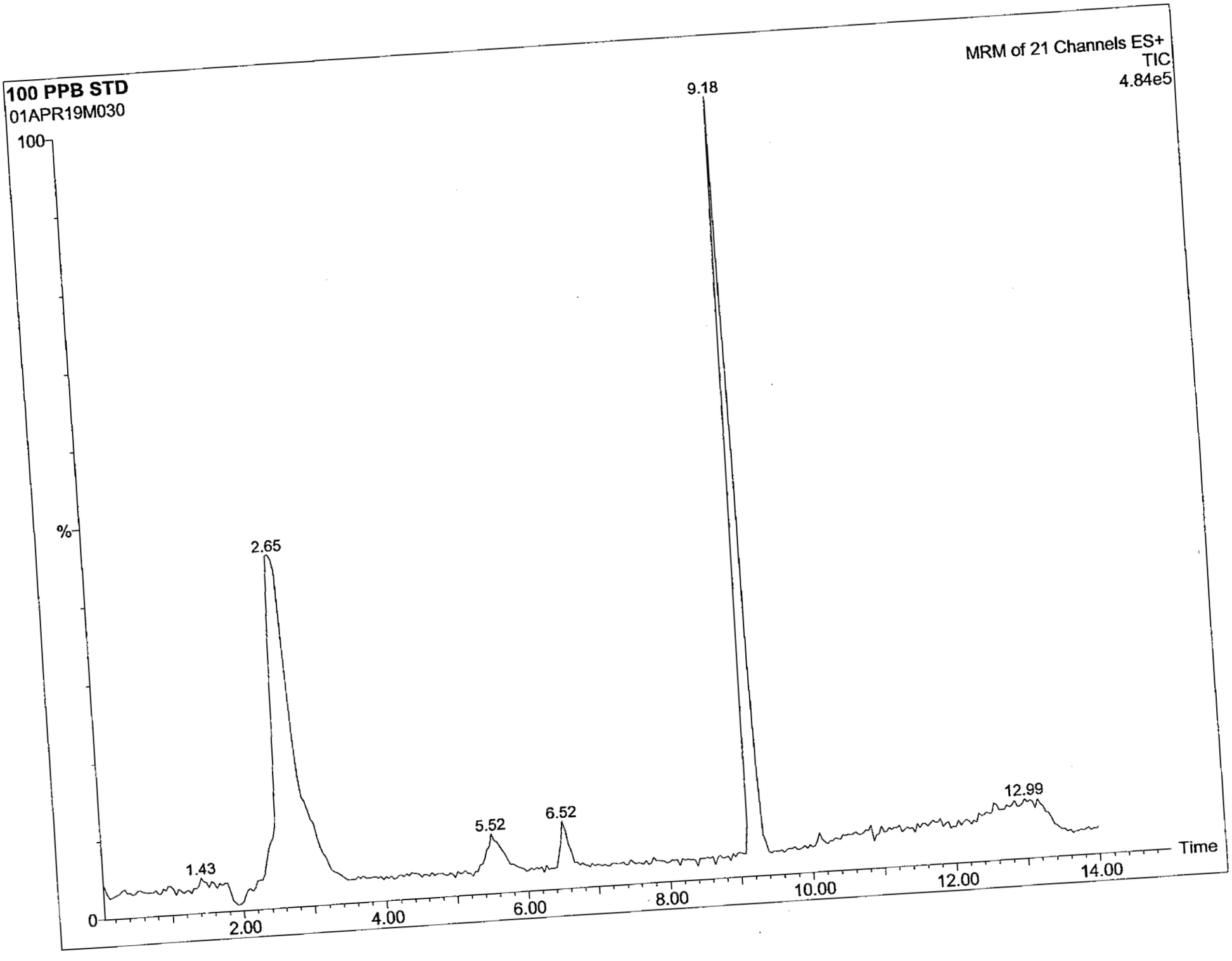

MBC - general daughter spectrum
01APR17A017 1 (0.043)
Daughters of 192ES+
1.29e5
100
%
0
m/z
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
28 29 33 42 43 51 53 58 59 64 65 66 68 79 80 82 89 90 92 93 104 105 106 115 117 118 130 132 133 135 149 157 157 160 162 165 179 184 189 190 192 194 197


MBC - 160 optimized
01APR17A018 49 (0.883)
Daughters of 192ES+
4.14e5
100
%
0
160
192
33
43
58
59
65
68
85
90
92
93
105
107
117
118
131
132
133
148
157
157
162
173
188
190
195
196
m/z
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200


MBC - 132 optimized
01APR17A019 49 (0.883)
Daughters of 192ES+
1.93e5
100
%
0
160
132
192
92
105
191
90
133
117
65
59
190
194
200
m/z
25 29 33 39 43 51 52 57 63 6669 79 80 82 89 93 104 106 116 118 131 134 145 147 156 157 162 174 179 187
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

Appendix C

Total Ion Chromatogram and Selected Ion Chromatograms for Target Analytes

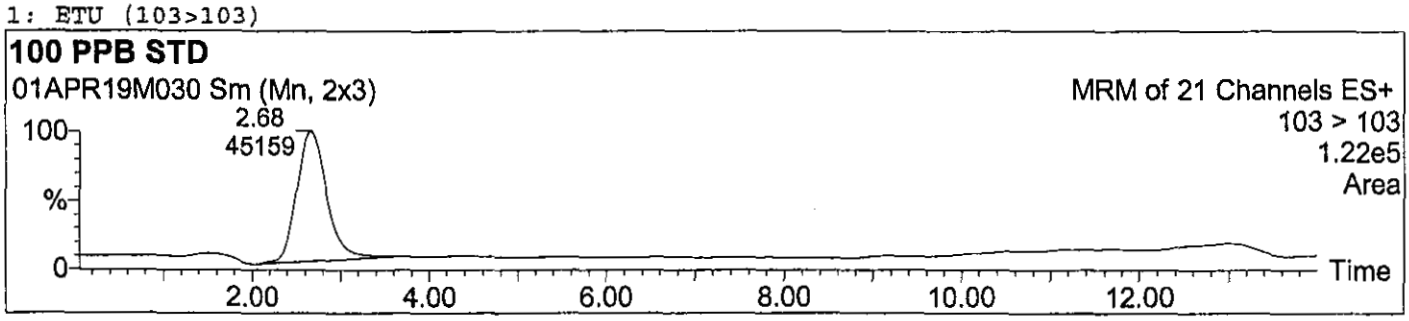

100 PPB STD
01APR19M030
MRM of 21 Channels ES+
TIC
4.84e5
100
%
0
9.18
2.65
1.43
5.52
6.52
12.99
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Time

Sample List: C:\MASSLYNX\lompoc.PRO\SampleDB\01APR19
Last modified: Fri Apr 20 08:33:23 2001
Method: C:\MASSLYNX\lompoc.PRO\MethDB\LOMPOC
Last modified: Fri Apr 20 08:48:31 2001
Job Code:

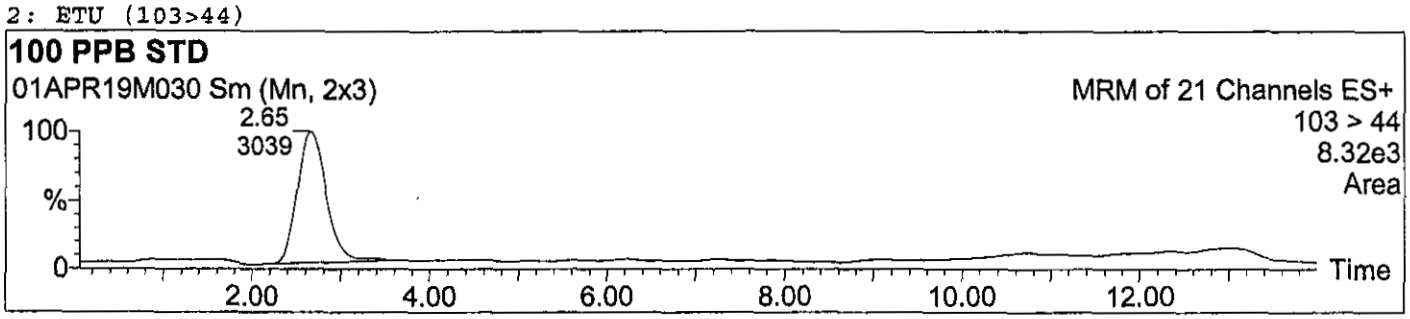
Printed: Fri Apr 20 08:49:25 2001

Name: 01APR19M030
Text: 100 PPB STD

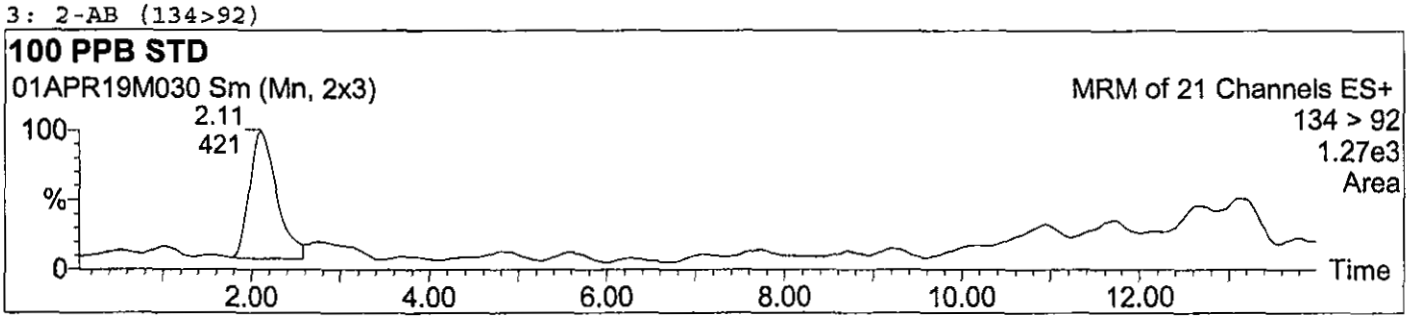
1: ETU (103>103)



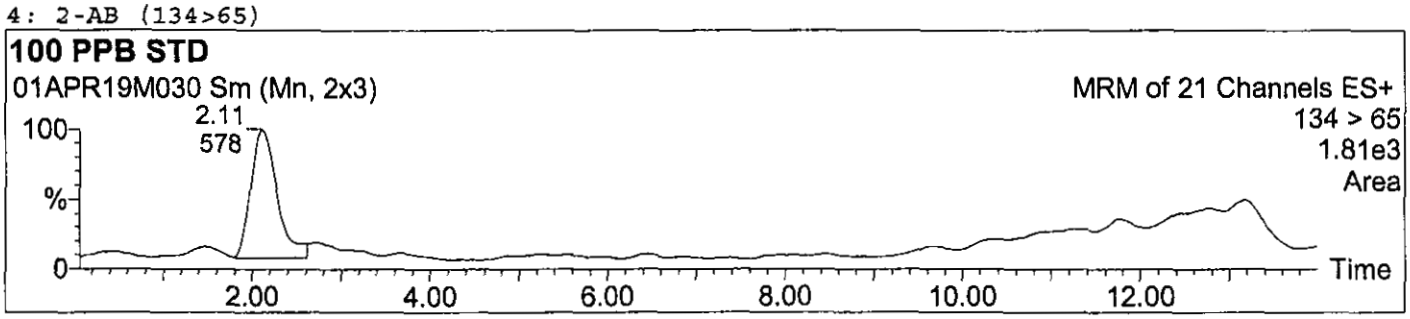
2: ETU (103>44)



3: 2-AB (134>92)



4: 2-AB (134>65)

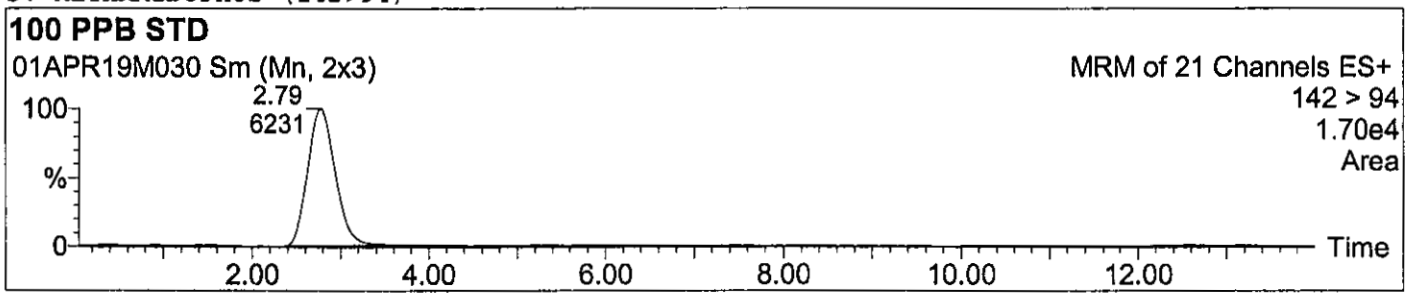


Sample List: C:\MASSLYNX\lompoc.PRO\SampleDB\01APR19
Last modified: Fri Apr 20 08:33:23 2001
Method: C:\MASSLYNX\lompoc.PRO\MethDB\LOMPOC
Last modified: Fri Apr 20 08:48:31 2001
Job Code:

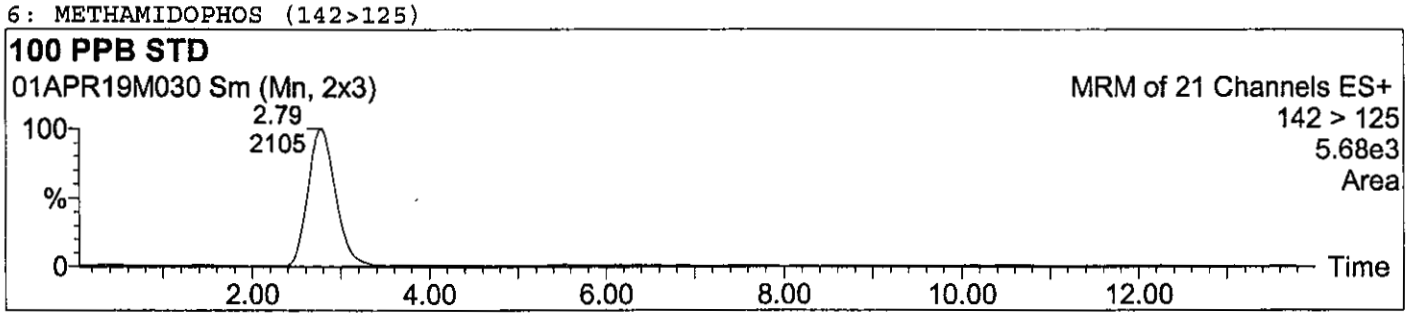
Printed: Fri Apr 20 08:49:25 2001

Name: 01APR19M030
Text: 100 PPB STD

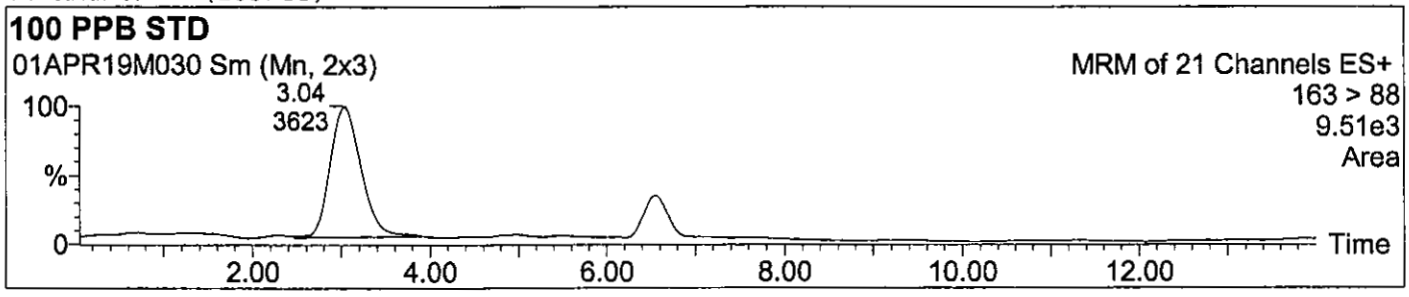
5: METHAMIDOPHOS (142>94)



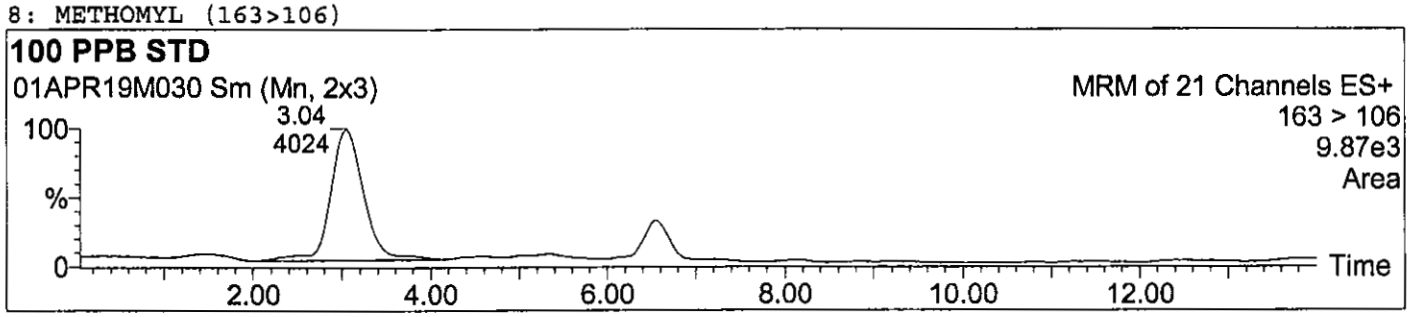
6: METHAMIDOPHOS (142>125)



7: METHOMYL (163>88)



8: METHOMYL (163>106)

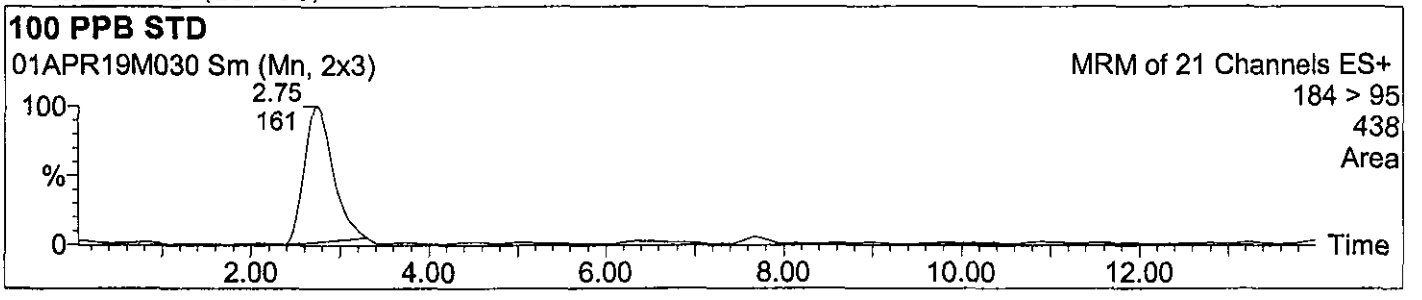


Sample List: C:\MASSLYNX\lompoc.PRO\SampleDB\01APR19
Last modified: Fri Apr 20 08:33:23 2001
Method: C:\MASSLYNX\lompoc.PRO\MethDB\LOMPOC
Last modified: Fri Apr 20 08:48:31 2001
Job Code:

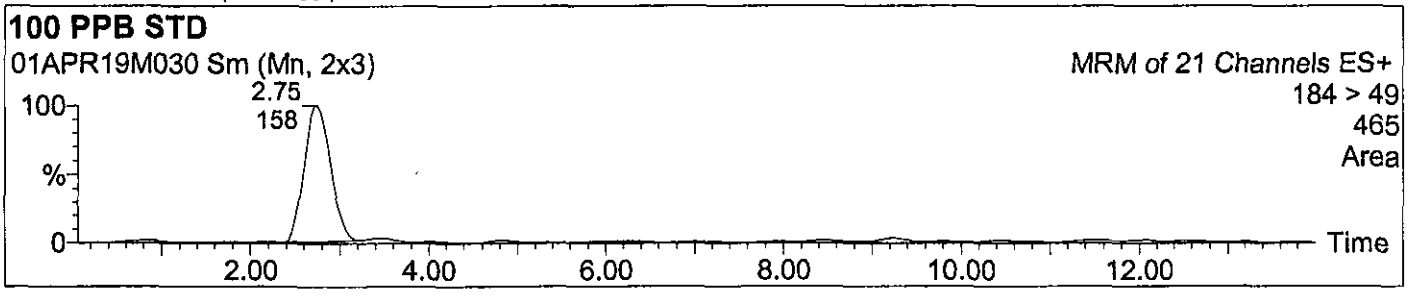
Printed: Fri Apr 20 08:49:25 2001

Name: 01APR19M030
Text: 100 PPB STD

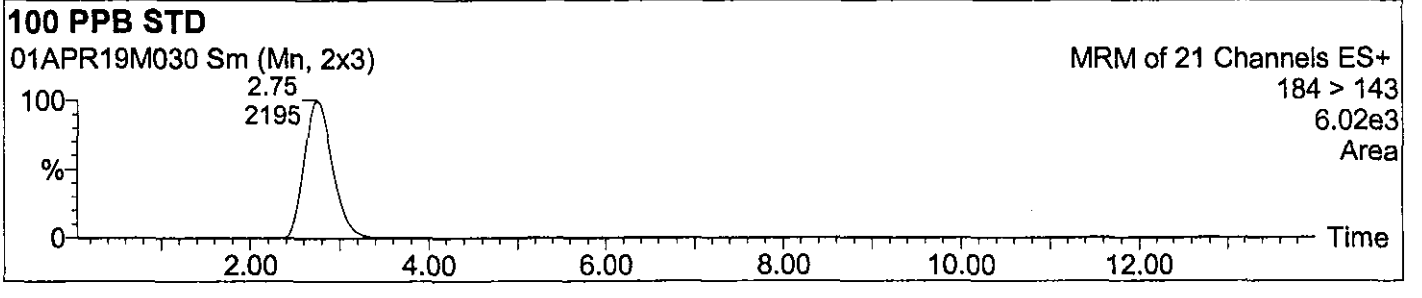
9: ACEPHATE (184>95)



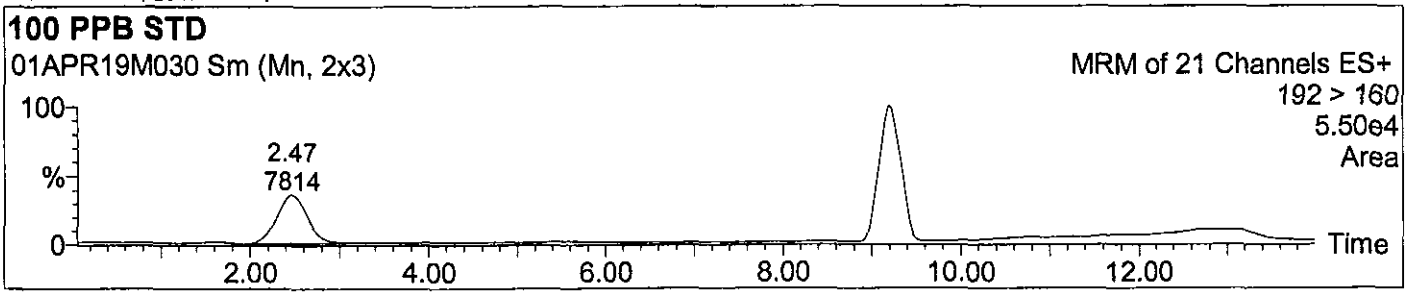
10: ACEPHATE (184>49)



11: ACEPHATE (184>143)



12: MBC (192>160)

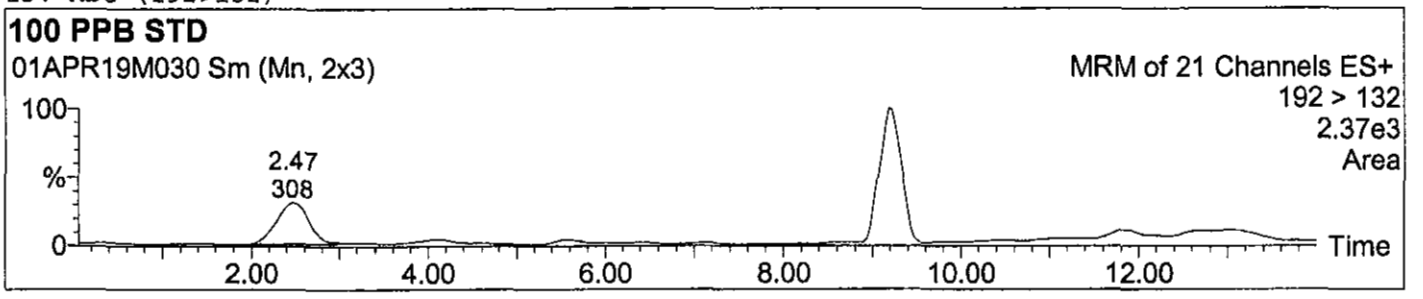


Sample List: C:\MASSLYNX\lompoc.PRO\SampleDB\01APR19
Last modified: Fri Apr 20 08:33:23 2001
Method: C:\MASSLYNX\lompoc.PRO\MethDB\LOMPOC
Last modified: Fri Apr 20 08:48:31 2001
Job Code:

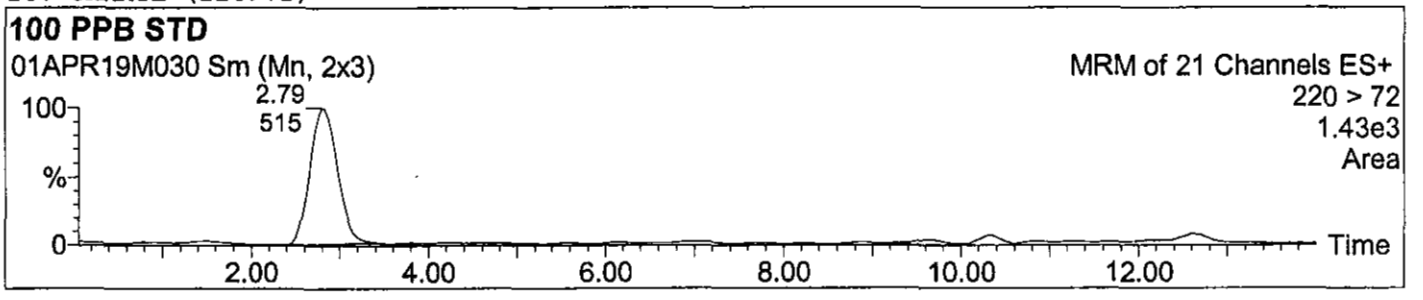
Printed: Fri Apr 20 08:49:25 2001

Name: 01APR19M030
Text: 100 PPB STD

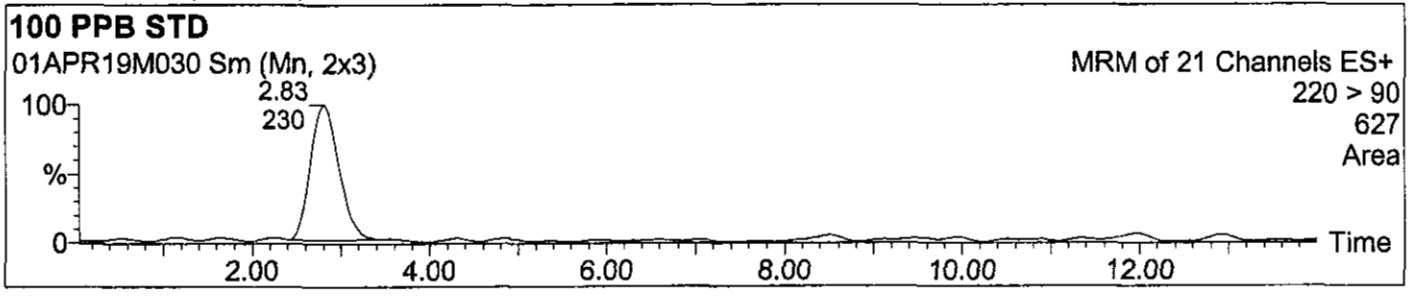
13: MBC (192>132)



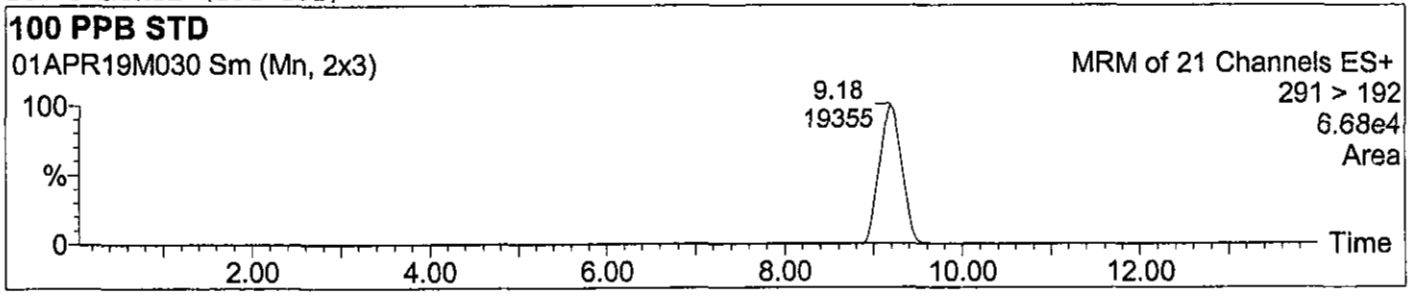
14: OXAMYL (220>72)



15: OXAMYL (220>90)



16: BENOMYL (291>192)



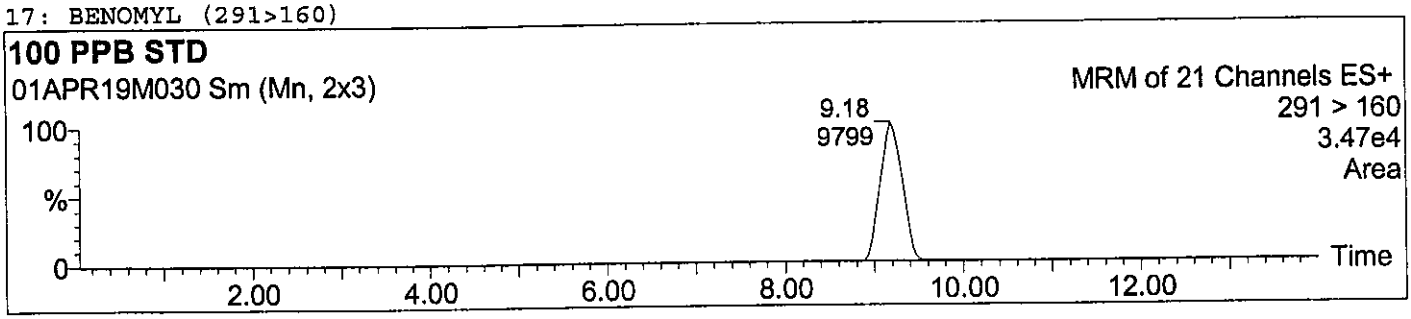
Quantify Sample Report

Sample List: C:\MASSLYNX\lompoc.PRO\SampleDB\01APR19
Last modified: Fri Apr 20 08:33:23 2001
Method: C:\MASSLYNX\lompoc.PRO\MethDB\LOMPOC
Last modified: Fri Apr 20 08:48:31 2001
Job Code:

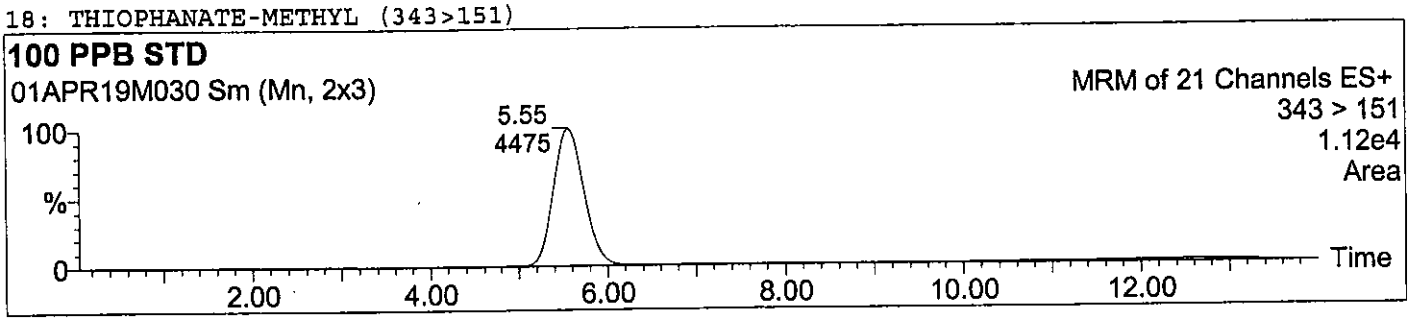
Printed: Fri Apr 20 08:49:25 2001

Name: 01APR19M030
Text: 100 PPB STD

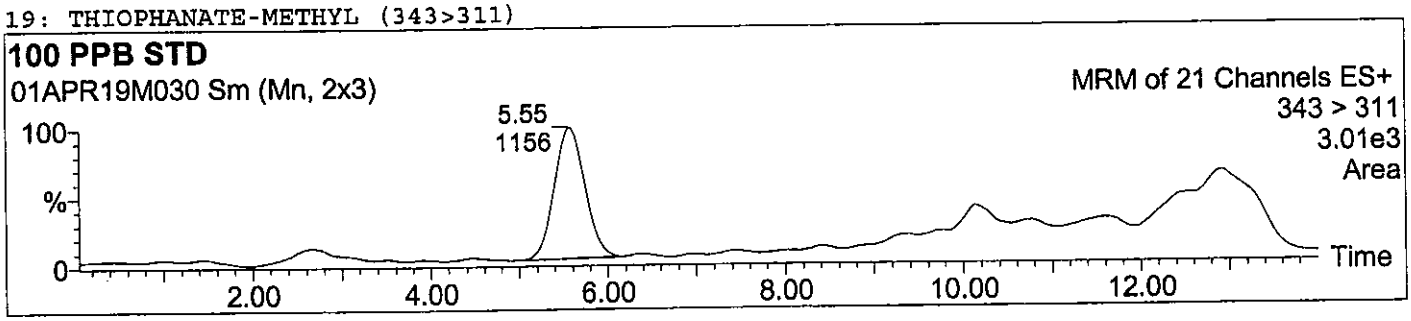
17: BENOMYL (291>160)



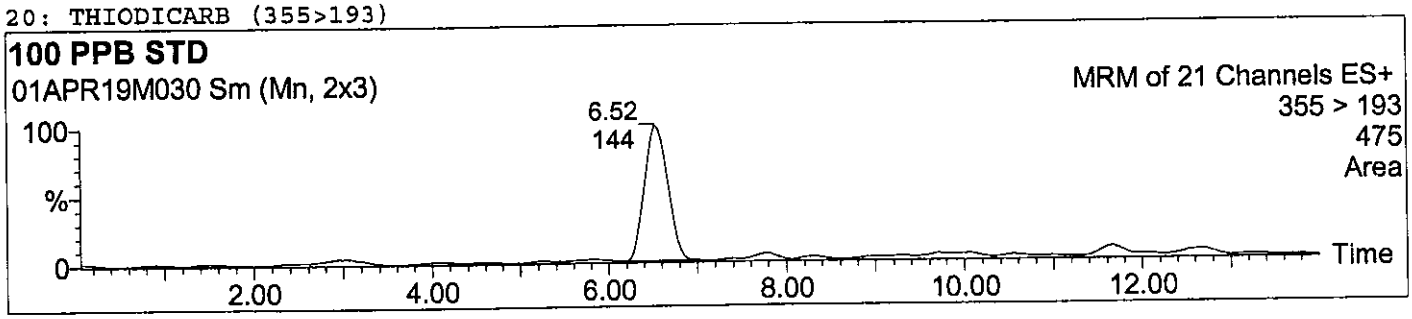
18: THIOPHANATE-METHYL (343>151)



19: THIOPHANATE-METHYL (343>311)



20: THIODICARB (355>193)

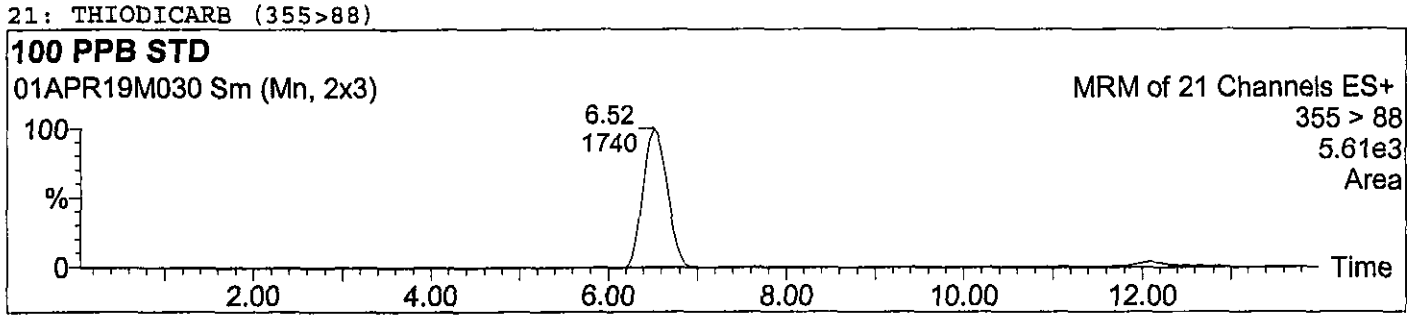


Sample List: C:\MASSLYNX\lompoc.PRO\SampleDB\01APR19
Last modified: Fri Apr 20 08:33:23 2001
Method: C:\MASSLYNX\lompoc.PRO\MethDB\LOMPOC
Last modified: Fri Apr 20 08:48:31 2001
Job Code:

Printed: Fri Apr 20 08:49:25 2001

Name: 01APR19M030
Text: 100 PPB STD

21: THIODICARB (355>88)



#	Name	Scan	RT	Area	Response	Flags	ng/mL
1	ETU (103..	74	2.681	45159	45158.813	bb	
2	ETU (103..	73	2.646	3039	3038.771	bb	
3	2-AB (13..	58	2.108	421	421.099	bd	
4	2-AB (13..	58	2.108	578	578.456	bd	
5	METHAMID..	77	2.791	6231	6230.886	bb	
6	METHAMID..	77	2.791	2105	2104.744	bd	
7	METHOMYL..	84	3.044	3623	3623.050	db	
8	METHOMYL..	84	3.044	4024	4023.817	bb	
9	ACEPHATE..	76	2.755	161	160.997	bb	
10	ACEPHATE..	76	2.755	158	158.232	bb	
11	ACEPHATE..	76	2.755	2195	2194.657	bb	
12	MBC (192..	68	2.466	7814	7813.620	bb	
13	MBC (192..	68	2.466	308	308.333	bb	
14	OXAMYL (..	77	2.791	515	514.925	bb	
15	OXAMYL (..	78	2.826	230	230.352	bb	
16	BENOMYL ..	255	9.184	19355	19354.600	bb	
17	BENOMYL ..	255	9.184	9799	9798.940	bb	
18	THIOPHAN..	154	5.554	4475	4474.954	bb	
19	THIOPHAN..	154	5.554	1156	1156.259	bb	
20	THIODICA..	181	6.523	144	144.338	bb	
21	THIODICA..	181	6.523	1740	1739.928	bb	